ADSORPTION STUDIES ON SOME NATURAL BIOSORBENTS: REMOVAL OF HEAVY METALS FROM WATER

DISSERTATION

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Certificate

*This is to certify that the dissertation entitled "**Adsorption studies on some natural biosorbents: Removal of heavy metals from water**" being submitted by **Ms. Amna Khatoon** for the partial fulfillment of the requirements for the award of **M.Phil.** Degree in Applied Chemistry at the Aligarh Muslim University, Aligarh, is an authentic work carried out by her under my supervision and guidance. To the best of my knowledge, the matter embodied in the dissertation has not been submitted to any other University or Institute for the award of a degree.*

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DISSERTATION

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A Khatoon

(Amna Khatoon)

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NOMENCLATURE

BIS	Bureau of Indian Standard
ICMR	Indian council of medical research
CPCB	Central Pollution Control Board
USEPA	United States Environment Protection Agency
AAS	Atomic Absorption Spectrophotometer
TAFP	*Terminalia arjuna* fruit powder
C_e	Equilibrium concentration of adsorbate in the solution ($mg.L^{-1}$)
C_o	Initial concentration of adsorbate in the solution ($mg.L^{-1}$)
C_{Ac}	Equilibrium concentration of adsorbate on the adsorbent surface ($mg.L^{1}$)
C	Amount of adsorbate in the solution ($mg.L^{-1}$)
q_e	Amount of adsorbate adsorbed per unit weight of adsorbent at equilibrium or adsorption capacity ($mg.g^{-1}$)
m	Amount of adsorbent (g)
DDW	Double Distilled Water
FTIR	Fourier transform infrared spectroscopy
SEM	Scanning electron microscopy
$\Delta G°$	Standard Free energy change ($kJ.mole^{-1}$)
$\Delta H°$	Standard Enthalpy change ($kJ.mole^{-1}$)
$\Delta S°$	Standard Entropy change ($kJ.mole^{-1}.K^{-1}$)
$q_{e(exp)}$	Experimental value($mg.g^{-1}$)
$q_{e(cal)}$	Calculated value($mg.g^{-1}$)
K_1	Pseudo- first-order rate constant (min^{-1})
K_2	Pseudo-second-order rate constant ($g.mg^{-1}.min^{-1}$)
K_c	Equilibrium constant
b	Langmuir constant for energy of adsorption ($L.mg^{-1}$)
q_m	Monolayer adsorption capacity ($mg.g^{-1}$)
K_f	Freundlich adsorption constant ($mg.g^{-1}$) $(L.mg^{-1})^{1/n}$
n	Freundlich exponent
A	Temkin constant for Adsorption potential ($g.L^{-1}$)
B	Temkin constant for heat of adsorption ($J.mol^{-1}$)

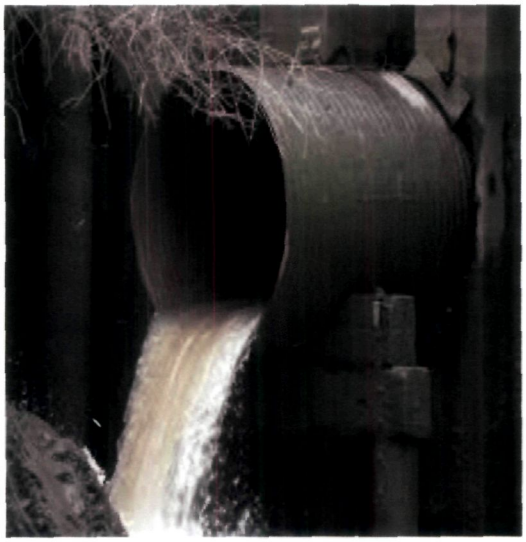
β	Constant related to the adsorption energy ($mol.K^{-2}.J^{-2}$)
ε	Polanyi potential
E	Mean free energy ($kJ.mol^{-1}$)
pHz	Point of zero charge
R	Universal gas constant (8.314 $J.mol^{-1}.K^{-1}$)
T	Absolute temperature (K)
t	Time (min)
V	Volume of solution (litre)

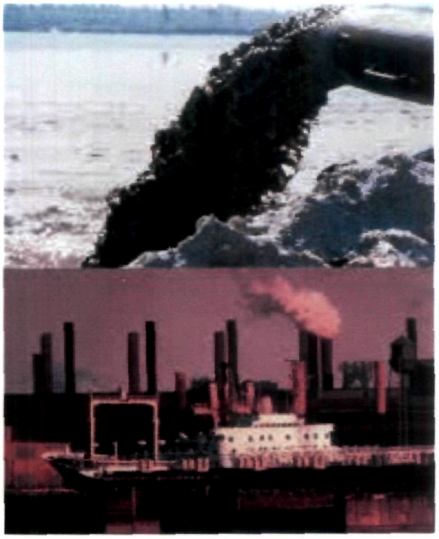
UNITS

°C	Degree Celsius
cm	Centimeter
g	Gram
$g.mg^{-1}.min^{-1}$	Gram per milligram-minute
h	Hours
$J.mol^{-1}.K^{-1}$	Joule per mole per kelvin
$kJ.mole^{-1}.K^{-1}$	Kilo Joules per mole-Kelvin
K	Kelvin
$kJ.mol^{-1}$	Kilo joule per mole
$L.mg^{-1}$	Litre Per milligram
$g.L^{-1}$	gram per Litre
$mg.L^{-1}$	Milligram per litre
min	Minute
mL	Millilitre
$mole.L^{-1}$	Moles per litre
$mg.g^{-1}$	Milligram per gram
min^{-1}	Per minute
rpm	Revolutions per minute
µg	Microgram

SUMMARY

The present work explored the adsorption potential of Terminalia arjuna fruit powder (TAFP) for the removal of heavy metals from aqueous solution. The maximum adsorption was observed for Pb(II), followed by Zn(II), Ni(II) and Cd (II). Effect of concentration, contact time, pH, adsorbent dose and temperature were studied by using batch process to optimize conditions for maximum adsorption. The adsorption of Pb (II) was concentration dependent. Kinetic data showed that the pseudo-second-order model provided the best fit for the experimental data and it was found that intra-particle diffusion was not the only rate-controlling factor but some other process like film diffusion was also involved in the adsorption. Thermodynamic parameters (ΔH^{o} and ΔG^{o}) suggested endothermic and spontaneous nature of adsorption. Mean free energies at different temperatures were in between 10.1 and 14.3 $kJ.mol^{-1}$ indicating chemical nature of adsorption process. Equilibrium isotherm data were analyzed using Langmuir, Freundlich, Temkin and Dubinin–Radushkevich (D–R) isotherms models at 30, 40 and 50°C. The breakthrough and exhaustive capacities were found to be 5 and 15 $mg.g^{-1}$ respectively. Desorption studies were carried out by column method and 84% of Pb (II) ions were recovered when 0.05 M HCl was used as desorbing solution.





CHAPTER -1

Introduction

1. INTRODUCTION

1.1. Environmental pollution

Pollution is an undesirable change in the physical, chemical or biological characteristics of air, water and soil that may harmfully affect the life or create a potential health hazard to any living organism. Pollution is thus direct or indirect changes in any component of the biosphere that is harmful to the living component(s), and in particular undesirable for man, affecting adversely the industrial progress, cultural and natural assets or general environment.

Environmental pollution is a major hazard facing the world today and there is an increasing awareness of the fact that a clean environment is necessary for smooth living and the better health of human beings. On account of the various activities of man, the composition and complex nature of environment gets changed. These activities include industrialization, construction, transportation etc. Such activities, although desirable for human development and welfare, lead to generation and release of objectionable materials into the environment thus turning it foul, and rendering our life miserable. Thus, pollution is a necessary evil of all development. The natural environment is clean, but due to multiferious activities of man it gets polluted resulting in what is called as environmental pollution. Fig. 1.1 illustrates how various gaseous pollutants enter into the air and leading to the pollution of other components of environment such as soil and water. Harmful pollutants present in the air enter into water and soil through wet deposition thus polluting them also.

Over the last three decades there has been increasing global concern over the public health impacts attributed to environmental pollution [Kimani, 2007], Human exposure to pollution is believed to be more intense now than at any other time in human existence [Schell et al, 2006]. Pollution can be made by human activity and by natural sources as well [Fereidoun et al, 2007].

The water we drink is essential ingredients for our wellbeing and a healthy life. Unfortunately polluted water is common throughout the world [European Public Health Alliance, 2009]. The WHO states that one sixth of the world's population, approximately 1.1 billion people do not have access to safe water and 2.4 billion lack basic sanitation [European Public Health Alliance, 2009]. Polluted water causes

various health hazards, death of human being, threatened aquatic life and also disturbs the production of different crops [Ashraf et al, 2010; Scipeeps, 2009]. In fact, the effects of water pollution are said to be the leading cause of death for humans across the globe. Moreover, water pollution affects our oceans, lakes, rivers, and drinking water, making it a widespread and global concern [Scipeeps, 2009]. Pollution of water by toxic metals has been accelerated dramatically since the beginning of the industrial revolution [Wu et al, 2009]

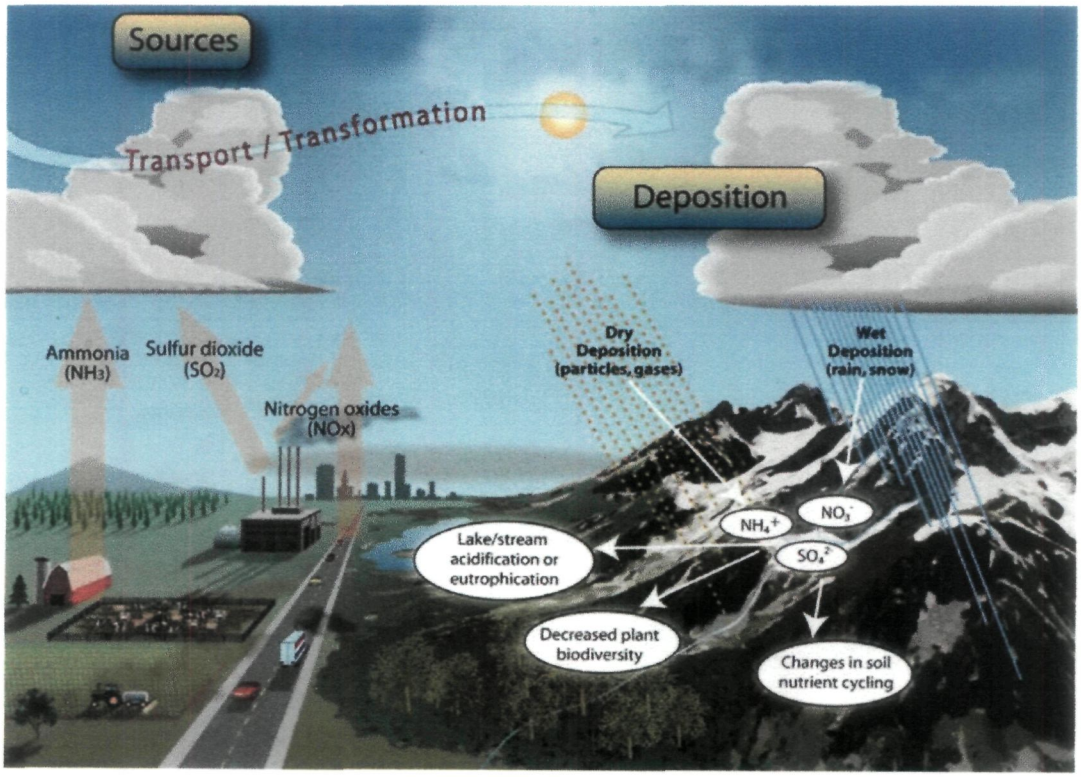


Fig 1.1: Pollutants Sources, Transport, Transformation, Deposition and Effects

[source: google images]

1.2. CLASSIFICATION OF POLLUTION

Environmental pollution may be classified as follows

- Air pollution
- Soil pollution
- Thermal pollution
- Water pollution

1.2.1. Air pollution

The origin of air pollution on the earth can be traced from the times when man started using firewood as a means of cooking and heating. With the discovery and increasing use of coal, air pollution became more pronounced especially in urban areas. Air pollution occurs due to the presence of undesirable solid or gaseous particles in the air in quantities that are harmful to human health and the environment. Air may get polluted by natural sources such as volcanoes, forest fires etc. or by human activities such as combustion of fuels for cooking and heating purposes, emmission from industries, automobiles, power generation, smelting, mining etc. The main pollutants found in the air include, particulate matter, lead, ground-level ozone, heavy metals, sulphur dioxide, benzene, carbon monoxide and nitrogen dioxide [European Public Health Alliance, 2009]. Rapid growth in urban population, increasing industrialization, and rising demands for energy and motor vehicles are worsening the air pollution levels. Other factors, such as poor environmental regulation, less efficient technology of production, congested roads, and poor maintenance of vehicles, also add to the problem [Mishra, 2003].

1.2.2. Soil pollution

Soil sustains all life on earth. Roots of plants grow in the soil and absorb nutrients from it. Soil is one of the important and valuable resources of the nature. [Khakbaz et al, 2012]. Domestic, municipal, industrial and agricultural wastes are the main source of soil poluution. Addition of excessive chemical fertilizers to the soil in order to increase the crop yield, irrigation of agricultural field with polluted water, dumping of toxic waste, deforestation, discharge of industrial effluent etc., all these activities contaminate the soil to a greater extent [Kimani, 2007]. Among all chemical

pollutants, it seems that rare elements and heavy metals have had specific ecological, biological and/or health effects on the environment of organisms living on the earth. Resistance and reliability of heavy metals in soil is very long than other pollutants and soil pollution by the heavy metals is relatively permanent [Khakbaz et al, 2012]. Soil pollution results when wastes are not disposed in a regulated and proper manner. Rubbish should be placed in disposal containers for collection and dumped in landfills that are covered with soil. Exposed litter is the breeding ground for rats, mosquitoes and flies, apart from being unsightly, unhygienic and a danger to animals and plants. Toxic chemicals must be disposed off in sealed containers that are buried in special cemented landfills.

1.2.3. Thermal pollution

It may be defined as the warming up of aquatic ecosystem to the point where the desireable organisms are adversely affected. Temperature increase of even one to two degree celcius can cause significant changes in organism's metabolism. Thermal pollution may also increase the enzyme activity of aquatic animals [Goel, 2005]. The accelerated pace of development, rapid industrialization and extensive population density have increased demand of thermal power plants. Main sources of thermal pollution are these thermal power plants which include nuclear power plants, coal fired power plants, hydroelectric power plants. Harmful effects of thermal pollution include reduction in dissolved oxygen, changes in water properties, increase in water toxicity, interference with biological activities, increase vulnerability to diseases and undesirable changes in algae production.

1.2.4. Water pollution

Water pollution is the introduction of chemical, physical, or biological agents into water that degrade water quality and adversely affect the organisms that depend on the water [Mukesh Kumar Mishra]. Water is one of the most important and basic natural resources. Water is not only one of the most essential commodities of our day-to-day life, but the development of this natural resource also plays a crucial role in economic and social development processes [CPCB, 2007].

Although 71% of the earth's surface is covered by water of which about 97% is found in oceans and is too salty for drinking or irrigation. The remaining 3% is fresh water, of this 2.997% is locked in ice caps or glaciers. Thus only 0.003% of the earth' total volume of water is available to us as soil moisture, groundwater, water vapour and water in lakes, streams, rivers and wetlands. The WHO states that one sixth of the world's population; approximately 1.1 billion people do not have access to safe water and 2.4 billion lack basic sanitation [European Public Health Alliance, 2009].

Water pollution has many sources. The most polluting of them are the city sewage and industrial waste discharged into the rivers. The facilities to treat waste water are not adequate in any city in India. Presently, only about 10% of the wastewater generated is treated; the rest is discharged as it is into our water bodies. Due to this, pollutants enter groundwater, rivers, and other water bodies. Such water, which ultimately ends up in our households, is often highly contaminated and carries disease-causing microbes. Agricultural run-off, or the water from the fields that drains into rivers, is another major water pollutant as it contains fertilizers and pesticides. Polluted water causes various health hazards, threatened aquatic life and also disturbs the production of different crops [Ashraf et al, 2010; Scipeeps, 2009]. In fact, the effects of water pollution are said to be the leading cause of death for humans across the globe. Moreover, water pollution affects oceans, lakes, rivers, and drinking water, making it a widespread and global concern [Scipeeps, 2009]. Water pollution is a major global problem which requires ongoing evaluation and revision of water resource policy at all levels (international down to individual aquifers and wells). It has been suggested that it is the worldwide leading cause of deaths and diseases and accounts for more than 14,000 deaths daily [Pink et al, 2006].

1.2.4.1. Sources of water pollution

The two main sources of water pollution are;

- Point source
- Non point or diffuse source

Point source

Harmful substances come directly into a water body from an identifiable single source. Examples of point sources are;

- Leaking septic-tank systems.
- Leaking storage lagoons for polluted waste.
- Unlined landfills.
- Leaking underground storage tanks that contain chemicals or fuels such as gasoline.
- Polluted water from abandoned and active mines.
- Water discharged by industries.
- Public and industrial wastewater treatment plants.
- Effluent discharges from sewage treatment works and industrial sites, power stations.

Non-point or diffuse source

Pollutants enter indirectly into a water body from many different sources that are often difficult to identify. For example, a river can be polluted by runoff from any of the land in its watershed. If a farm, a road, or any other land surface in a watershed is polluted, runoff from a rainstorm can carry the pollution into a nearby river, stream, or lake. Some additional causes of nonpoint pollution are;

- Chemicals added to road surfaces (salt and other de-icing agents)
- Water runoff from city and suburban streets that may contain oil, gasoline, animal feces, and litter
- Pesticides, herbicides, and fertilizer from residential lawns, farmland etc.
- Feces and agricultural chemicals from livestock feedlots.
- Precipitation containing air pollutants.
- Soil runoff from farms and construction sites.
- Oil and gasoline from personal watercraft.

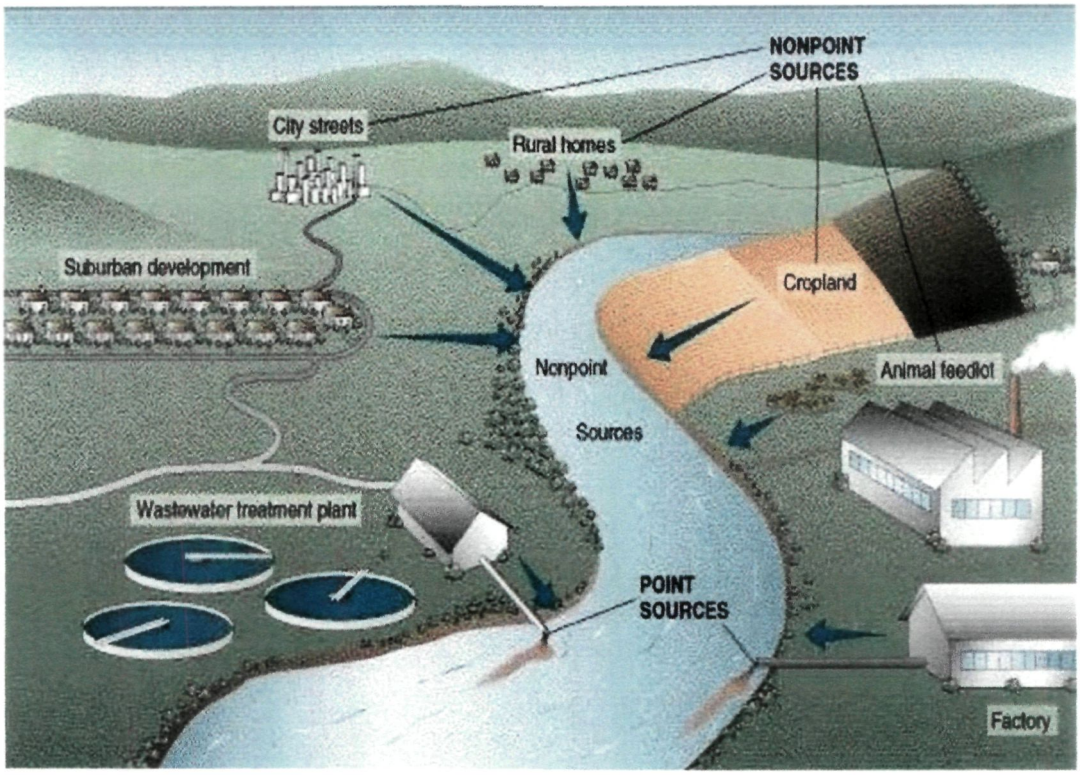


Fig 1.2: Point and Non point sources of water pollution [source: google images]

Table 1.1: Examples of sources of pollution and the potential pollutant discharged arising from point or non point sources [FWR, 2005]

Examples of sources of pollution	Point/Non point sources	Potential pollutants
Effluent discharges from sewage treatment work	Point source	Nitrogen(N) and phosphorus(P), persistent organic pollutants, pathogens, solids, litter
Industrial effluent discharges	Point source	N, oxygen depleting substances and a broad spectrum of chemicals
Industrial processes	Point source	broad spectrum of chemicals released to air and water
Oil storage facilities	Point source	Hydrocarbons
Urban stormwater discharges	point source	N, P, oxygen depleting substances, persistent organic pollutants, heavy metals, Hydrocarbons, pathogens, suspended solids, litter
Landfill sites	Point source	N, ammonia, oxygen depleting substances, broad spectrum of chemicals
Fish farming	Point source	N, P, oxygen depleting substances, pathogens
Pesticide use	Non point source	Broad spectrum of chemicals
Organic waste recycling to land	Non point source	N, P, pathogens
Agricultural fertilizers	Non point source	N, P
Soil culvitation	Non point source	Soil, N, P
Power generation facilities	Non point source	N, Sulphur
Farm wastes and silage	Point/non point source	N, P, oxygen depleting substances, pathogens
Contaminated land	Point/non point source	Hydrocarbons, organic chemicals, heavy metals, oxygen depleting substances
Mining	Point/non point source	heavy metals, acid mine drainage
Leaking pipelines	Point/non point source	Oil, sewage

1.2.4.2. Effects of water pollution

The effects of water pollution are not only devastating to people but also to animals, fish, and birds. Polluted water is unsuitable for drinking, recreation, agriculture, and industry. Eventually, it is a hazard to human health. Various diseases spreads by consumption of polluted water include typhoid, amoebiasis, diardiasis, ascariasis, hookworm, respiratory infections, hepatitis, encephalitis, gastroenteritis, diarrhea, vomiting, and stomach aches. It has been estimated that 50,000 people die daily world-wide as a result of water-related diseases [Gambhir et al, 2012]. Due to water pollution, the entire ecosystem gets disturbed. Unsafe drinking water, along with poor sanitation and hygiene, are the main contributors to an estimated 4 billion cases of diarrhoeal disease annually, causing more than 1.5 million deaths, mostly among children less than 5 years of age [WHO 2004]. Contaminated drinking water is also a major source of hepatitis, typhoid and opportunistic infections that attack the immuno-compromised, especially persons living with HIV/AIDS [UNICEF 2011]. Almost 1 billion people lack access to safe and improved water supply. More than 50 countries still report cholera to WHO (World Health Organization). Millions are exposed to unsafe levels of naturally occurring arsenic and fluoride in drinking water which leads to cancer and tooth/skeletal damage. An estimated 260 million people are infected with schistosomiasis [WHO 2004]. 1.3 million people die of malaria each year, 90% of whom are children under 5 [Gambhir et al, 2012]. Water pollution, apart from causing hazard to human health, also diminishes the aesthetic quality of lakes and rivers. More seriously, contaminated water destroys aquatic life and reduces its reproductive ability. In short nobody can escape the adverse effects of water pollution.

1.3. CLASSIFICATION OF WATER POLLUTANTS

Water pollutant may be broadly classified under the following categories;

1.3.1. Organic pollutants

1.3.2. Inorganic pollutants

1.3.3. Suspended solids and sediments

1.3.4. Radioactive materials

1.3.1. Organic Pollutants

Organic pollutants are the most common pollutants found in water. It is caused by naturally occurring compounds like protein, fats, carbohydrates etc. as well as synthetic compounds like dyes, pesticides etc. they are originated mainly from domestic sewage, urban runoff, industrial effluents (soaps, detergents, pesticides, herbicides), farm waste, petroleum hydrocarbons including fuels(gasoline, diesel fuels), lubricant fuel, and fuel combustion byproducts from storm water runoff [EPA, 2005]. These pollutants when discharged into water bodies, are degraded into simpler compounds by aerobic bacteria, making them less harmful. Aerobic bacteria consume dissolved O_2 present in water to degrade organic pollutants. The amount of O_2 required to oxidize a given quantity of organic material is called as biological oxygen demand (BOD). Due to the high discharge by the industries, BOD level increases leading to exhaustion of dissolved O_2 making aerobic bacteria die and thus entire aquatic ecosystem get disturbed [Burton et al, 2001].

1.3.2. Inorganic Pollutants

These includes sulphate, nitrates, phosphates, heavy metals, H_2SO_4, HNO_3, H_3PO_4 etc. which are obtained from mines, industrial discharge, i.e. tannery, plating and metallurgical operations, fertilizers found in storm water runoff, heavy metals from motor vehicles, industries and acid mine drainage [EPA, 2005]. Inorganic acids and alkali can do extensive damage to water bodies by breaking down into natural buffer system and altering its normal pH values. Changes in pH have a profound effect on aquatic organism especially fishes. Fresh water fishes and algae usually thrive in the pH range 5.0-8.5. Under more acidic and alkaline conditions, the aquatic

population tends to fall as they destroy aerobic bacteria with no supply of oxygen. Self purification property of water is also hindered by presence of heavy metals.

1.3.3. Suspended solids and Sediments

Due to natural erosion of rocks and soil, almost all the water bodies contain undissolved particles called sediments. Suspended matter mainly clays, silt, and pulverized rocks accumulate in the river which are harmless but when their concentration increases, they cause problems. Suspended matter in sewage effluents, dairy wastes and coal washery residue stones, quarrying stones contain chiefly inorganic suspended solids. Sediments cause problems by filling irrigation ditches and clogging harbors and lakes. Sediments and suspended particles exchange cations with the surrounding aquatic medium and act as depositories for trace metals such as Cu, Co, Ni, Mn, Cr and Mo [Schueler et al, 2000]. Suspended solids such as silt and coal may harm the gills of the fish and causes asphyxiation. When toxic substances like heavy metals and pesticides are released into turbid water, the toxins adhere to the suspended particles and become concentrated in sediments. The self purification system of water is also retarded due to the presence of sediments.

1.3.4. Radioactive Substances

Radioactive elements enter into water bodies due to various activities such as mining and processing of ores, increasing use of radioactive isotopes, radioactive materials from nuclear reactors and nuclear power plants. When these radionucleoides are taken up by aquatic organism, exchange takes place with chemically similar elements present in aquatic organisms for example, ex-radioactive strontium -90 and radium 226 replaces calcium, phosphorous-32 adsorbed by bones in aquatic animals. Water weeds tend to assimilate strontium-90 and radium 226 and causes hazardous effect on organisms.

1.4. HEAVY METAL POLLUTION

The term "heavy metals" refers to any metallic element that has a relatively high density and is toxic or poisonous even at low concentration [Lenntech, 2004]. "Heavy metals" is a general collective term, which applies to the group of metals and metalloids with atomic density greater than 4 $g.cm^{-3}$, or 5 times or more, greater than water [Duruibe, J. O. et al, 2007]. Heavy metals include lead (Pb), cadmium (Cd), zinc (Zn), mercury (Hg), arsenic (As), silver (Ag) chromium (Cr), copper (Cu) iron (Fe), and the platinum group elements.

Heavy metals occur as natural constituents of the earth crust, and are persistent environmental contaminants since they cannot be degraded or destroyed. To a small extent, they enter the body system through food, air, and water and bio-accumulate over a period of time [Lenntech, 2004; UNEP/GPA, 2004]. Heavy metals can be emitted into the environment by both natural and anthropogenic activities. Anthropogenic activities which lead to the emission of heavy metals into environment include mining, smelting, combustion of fossil fuels etc [UNEP /GPA, 2004]. Cadmium is released as a by- product of zinc (and occasionally lead) refining; lead is emitted during its mining and smelting activities, from automobile exhausts (by combustion of petroleum fuels treated with tetraethyl lead antiknock) and from old lead paints; mercury is emitted by the degassing of the earth's crust. It is also introduced into the environment through cosmetic products as well as manufacturing processes like making of sodium hydroxide. The sources of emission of various heavy metals is summarized in Table 1.2. Generally, metals are emitted during their mining and processing activities [Lenntech, 2004]. Environmental pollution by heavy metals is very prominent in areas of mining and old mine sites and pollution reduces with increasing distance away from mining sites. These metals are leached out and in sloppy areas, are carried by acid water downstream or run-off to the sea. Through mining activities, water bodies are most emphatically polluted. Wells located near mining sites have been reported to contain heavymetals at levels that exceed drinking water criteria [Duruibe, J. O. et al, 2007]. The permissible limits of some heavy metals as set by different agencies are shown in Table 1.3.

1.4.1. Effects of heavy metal on human health

Heavy metal pollution poses serious threat to both environment and human health. Humans are adversely affected by heavy metals as they tend to accumulate in the tissues and vital organs of living organism thereby causing various diseases and long term disorders [Loutseti et al, 2009]. Although individual metals exhibit specific signs of their toxicity, the following have been reported as general signs associated with cadmium, lead, arsenic, mercury, zinc, copper and aluminium poisoning: gastrointestinal (GI) disorders, diarrhoea, stomatitis, tremor, hemoglobinuria causing a rust–red colour to stool, ataxia, paralysis, vomiting, convulsion, depression and pneumonia when volatile vapours and fumes of heavy metal are inhaled (Fig 1.3) [Duruibe, J. O. et al, 2007]. The nature of effects could be toxic (acute, chronic or sub-chronic), neurotoxic, carcinogenic, mutagenic or teratogenic. Effect of various heavy metals on human health is given in Table 1.2.

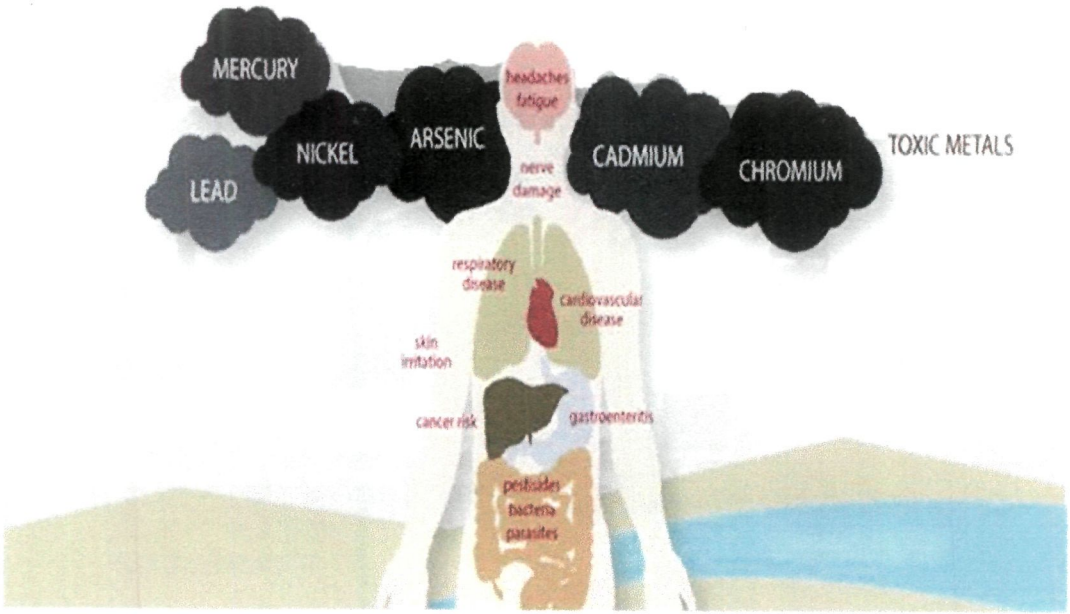
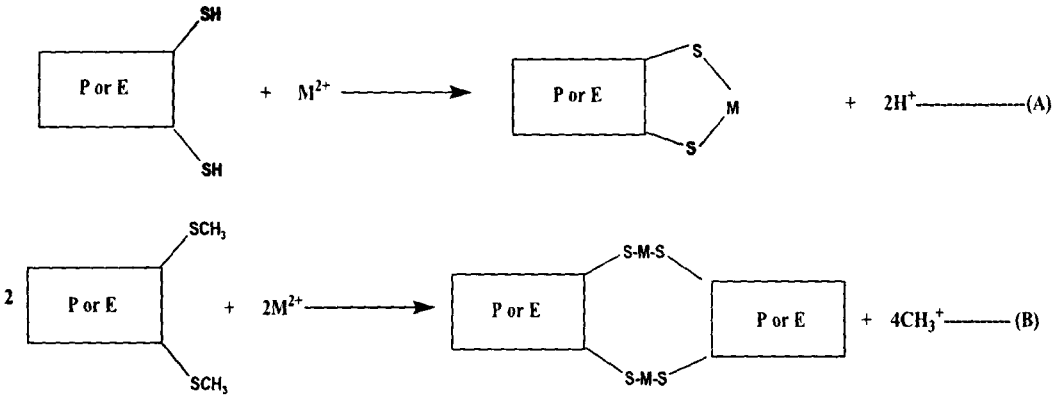


Fig 1.3: Effect of heavy metal on human health [source: google images]

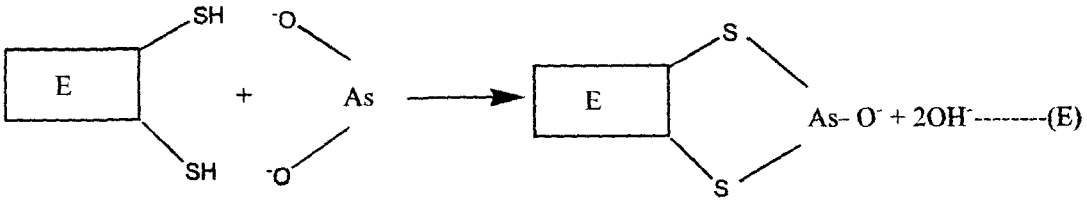
1.4.2. Biochemistry of metal toxicity

The poisoning effects of heavy metals are due to their interference with the normal body biochemistry in the normal metabolic processes. When ingested, in the acid medium of the stomach, they are converted to their stable oxidation states (Zn^{2+}, Pb^{2+}, Cd^{2+}, As^{2+}, As^{3+}, Hg^{2+} and Ag^{+}) and combine with the body's biomolecules such as proteins and enzymes to form strong and stable chemical bonds. The equations below show their reactions during bond formation with the sulphydryl groups (-SH) of cysteine and sulphur atoms of methionine (-SCH_3) [Ogwuegbu et al, 2003].



Where: (A) = Intramolecular bonding; (B) = Intermolecular bonding; P = Protein; E = Enzyme; M = Metal

The hydrogen atoms or the metal groups in the above case are replaced by the poisoning metal and the enzyme is thus inhibited from functioning. Furthermore, a metal ion in the body's metallo-enzyme can be conveniently replaced by another metal ion of similar size. Thus Cd^{2+} can replace Zn^{2+} in some dehydrogenating enzymes, leading to cadmium toxicity. In the process of inhibition, the structure of a protein molecule can be mutilated to a bio-inactive form, and in the case of an enzyme can be completely destroyed for example, toxic As^{3+} occurs in herbicide, fungicides and insecticides, and can attack –SH groups in enzymes to inhibit their bioactivities as shown below [Ogwuegbu et al, 2003].



The most toxic forms of these metals in their ionic species are the most stable oxidation states for example, Cd^{2+}, Pb^{2+}, Hg^{2+}, Ag^{+} and As^{3+}. In their most stable oxidation states, they form very stable biotoxic compounds with the body's bio-molecules, which become difficult to be dissociated, due to their bio-stabilities during extraction from the body by medical detoxification therapy [Duruibe, J. O. et al, 2007].

Table 1.2: Various heavy metals, their sources and effect on human health [De, 2010]

Heavy Metals	Sources	Disorders
Copper	Metal plating, industrial and domestic waste, mining, mineral leaching	Essential trace elements, not very toxic to animals, toxic to plants and algae at moderate levels
Chromium	Alloys, leather tanning, dyes and pigments and wood preservatives	Affects respiration (causing bleeding from nose), kidney and liver damage, stomach upsets, ulcers, convulsions and skin allergies, pneumonia, skin irritability..
Arsenic	Paints, rat poisoning, fungicides, wood preservatives. Also found in water supplies affecting the aquatic organisms.	Affects the blood, kidney, central nervous system, skin and digestive system.
Aluminium	food additives, antacids, buffered aspirin, astringents, nasal sprays, and antiperspirants; from drinking water; from automobile exhaust and tobacco smoke; and from using aluminum foil, aluminum cookware, cans, ceramics, and fireworks	Causes Alzheimir disease, degenerative muscular conditions and Cancer. Affects kidney, central nervous system.
Cadmium	Batteries, PVC plastics, paints pigments, insecticides,	Affects kidney, placenta, lungs brain, gastrointestinal system and

	fungicides, fertilizers, found in reservoir of shellfish, dental alloys, electroplating, automobile exhaust.	bones.
Mercury	Mining operations, chloroalkali, plants, thermometer, fungicide, paper industries, aquatic in food chains and fishes in lakes.	Affects brain and kidney
Nickel	Electroplating industries. Batteries, coins, stainless steel ,magnets.	Carcinogenic, causes skin allergies.
Iron	Drinking water, iron pipes, cookware.	Affects liver, kidney and cardiovascular system.
Lead	Batteries, paint pigments, PVC plastics, X-ray shielding, crystal glass production and pesticides.	Affects brain, kidney, blood and thyroid gland.
Cobalt	Burning of coal and oil. Found in soil, dust and seawater, car and truck exhaust.	Affects lungs causing asthma, cancer in animals, affects muscles.
Zinc	Zinc compounds are widely used in industry to make paint, rubber, dye, wood preservatives, and ointments. Also used for galvanizing sheet iron; as ingredient of alloys such as bronze, brass.	Inhalation of fumes exposed to zinc metal causes throat dryness, cough,, fever, nausea, vomiting, pancreas damage, lungs and stomach aches.
Barium	Paint, bricks, tiles, glass and rubber, drilling mud, oil industries.	Increases blood pressure, breathing problems, stomach irritation, brain swelling, muscle weakness and convulsive tremors.

Table 1.3: Permissible limits for heavy metals in drinking water as set by different agencies

Heavy metal	WHO ($mg.L^{-1}$)	USEPA ($mg.L^{-1}$)	BIS ($mg.L^{-1}$)	CPCB ($mg.L^{-1}$)	ICMR ($mg.L^{-1}$)
Lead (Pb^{2+})	0.05	0.05	0.1	No relaxation	0.05
Copper (Cu^{2+})	1.0	1.3	-	1.5	1.5
Chromium (Cr^{4+}, Cr^{3+}).	-	0.1	0.5	No relaxation	-
Arsenic (As^{3+})	0.05	0.05	0.05	No relaxation	0.05
Cadmium (Cd^{2+})	0.005	0.005	0.01	No relaxation	0.01
Mercury (Hg^{2+})	0.002	0.001	0.001	No relaxation	0.001
Zinc (Zn^{2+})	5.0	5.0	5.0	15.0	0.1

1.5. HEAVY METAL REMOVAL TECHNIQUES

1.5.1. Chemical precipitation

In chemical precipitation processes, chemicals react with heavy metal ions to form insoluble precipitates. The forming precipitates can be separated from the water by sedimentation or filtration and the treated water is then decanted and appropriately discharged or reused. The conventional chemical precipitation processes include hydroxide precipitation and sulfide precipitation. The most widely used chemical precipitation technique is hydroxide precipitation due to its relative simplicity, low cost and ease of pH control [Huisman et al., 2006]. A variety of hydroxides has been used to precipitate metals from wastewater. Based on the low cost and ease of handling, lime is the preferred choice of base used in hydroxide precipitation at industrial settings.

Sulfide precipitation is also an effective process for the treatment of toxic heavy metals ions. the sulfide precipitation process can achieve a high degree of metal removal over a broad pH range compared with hydroxide precipitation. Metal sulfide sludges also exhibit better thickening and dewatering characteristics than the corresponding metal hydroxide sludges. Chemical precipitation is usually adapted to treat wastewater containing high concentration of heavy metal ions but ineffective when metal ion concentration is low. Chemical precipitation is not economical and can produce large amount of sludge to be treated with great difficulties [Fenglian et al, 2011].

1.5.2. Ion exchange

Ion-exchange resin, either synthetic or natural solid resin, has the specific ability to exchange its cations with the metals in the wastewater. Among the materials used in ion-exchange processes, synthetic resins are commonly preferred as they are effective to remove the heavy metals from the solution [Alyüz et al, 2009]. The most common cation exchangers are strongly acidic resins with sulfonic acid groups (-SO_3H) and weakly acid resins with carboxylic acid groups (-COOH). Hydrogen ions in the sulfonic group or carboxylic group of the resin can serve as exchangeable ions with metal cations. As the solution containing heavy metal passes through the cation

exchange column, metal ions are exchanged for the hydrogen ions of the resin with the following ion-exchange process;

$$nR\text{—}SO_3H + M^{n+} \rightarrow (R\text{—}SO_3^-)_n M^{n+} + nH^+$$

$$nR\text{—}COOH + M^{n+} \rightarrow (R\text{—}COO^-)_n M^{n+} + nH^+$$

The uptake of heavy metal ions by ion-exchange resins is affected by certain variables such as pH, temperature, initial metal concentration and contact time [Gode et al. 2006]. Ionic charge also plays an important role in ion-exchange process. The major drawback in using ion-exchange resins is that they must be regenerated by chemical reagents when they are exhausted and the regeneration can cause serious secondary pollution. The process is expensive, especially when treating a large amount of wastewater containing heavy metal in low concentration, so they cannot be used at large scale [Fenglian et al, 2011].

1.5.3. Membrane filtration

Membrane filtration technologies with different types of membranes show great promise for heavy metal removal for their high efficiency, easy operation and space saving. The membrane processes used to remove metals from the wastewater are ultrafiltration, reverse osmosis, nanofiltration and electrodialysis.

1.5.3.1. Ultrafiltration

Ultrafiltration (UF) is a membrane technique working at low transmembrane pressures for the removal of dissolved and colloidal material. Since the pore sizes of UF membranes are larger than dissolved metal ions in the form of hydrated ions or as low molecular weight complexes, these ions would pass easily through UF membranes. To obtain high removal efficiency of metal ions, the micellar enhanced ultrafiltration (MEUF) and polymer enhanced ultrafiltration (PEUF) was proposed. MEUF was first introduced by Scamehorn et al. in the 1980s for the removal of dissolved organic compounds and multivalent metal ions from aqueous streams [Landaburu-Aguirre et al., 2009]. This separation technique is based on the addition of surfactants to wastewater. Metal removal efficiency by MEUF depends on the characteristics and concentrations of the metals and surfactants, solution pH, ionic strength, and parameters related to membrane operation. PEUF uses water-soluble

polymer to complex metallic ions and form a macromolecular, having a higher molecular weight than the molecular weight cut off of the membrane. The main parameters affecting PEUF are metal and polymer type, the ratio of metal to polymer, pH and existence of other metal ions in the solution [Fenglian et al, 2011].

1.5.3.2. Reverse osmosis

The reverse osmosis (RO) process uses a semi-permeable membrane, allowing the fluid that is being purified to pass through it, while rejecting the contaminants. RO is one of the techniques able to remove a wide range of dissolved species from water. It accounts for more than 20% of the world's desalination capacity [Shahalam et al., 2002]. Pre-treatment steps of effluents water before going for reverse osmosis process is necessary and usually this is made possible by using ultra filtration to first remove large molecules and colloidal materials so that this will help to protect the membranes. The spiral wound configuration of the membranes support structure proves to be the best and most effective in use when it comes to municipal wastewater reclamation. However, problems that are still needed to be solved are [Fenglian et al, 2011] membrane durability problems, fouling of membrane, sensitive to hard water salts.

1.5.3.3. Nanofiltration

Nanofiltration (NF) is the intermediate process between UF and RO. NF technology has been used for the rejection of heavy metal ions such as nickel [Murthy et al., 2008], chromium [Muthukrishnan et al., 2008], copper [Cséfalvay et al., 2009; Ahmad et al., 2010] and arsenic [Nguyen et al., 2009; Figoli et al., 2010] from wastewater.

1.5.3.4. Electrodialysis

Electrodialysis (ED) is another membrane process for the separation of ions across charged membranes from one solution to another using an electric field as the driving force. In most ED processes, ion-exchange membranes are used. The membranes are actually of two basic types: cation-exchange and anion-exchange membranes. This process has been widely used for the production of drinking and process water from brackish water and seawater, treatment of industrial effluents, recovery of useful materials from effluents and salt production [Sadrzadeha et al.,

2009]. Membrane filtration technology can remove heavy metal ions with high efficiency, but its problems such as high cost, process complexity, membrane fouling and low permeate flux have limited their use in heavy metal removal [Fenglian et al. 2011].

1.5.4. Coagulation and flocculation

Coagulation and flocculation followed by sedimentation and filtration is also employed to remove heavy metal from wastewaters. Coagulation is the destabilization of colloids by neutralizing the forces that keep them apart. Many coagulants are widely used in the conventional wastewater treatment processes such as aluminum, ferrous sulfate and ferric chloride, resulting in the effective removal of wastewater particulates and impurities by charge neutralization of particles and by enmeshment of the impurities on the formed amorphous metal hydroxide precipitates. Generally, coagulation-flocculation can't treat the heavy metal wastewater completely [Chang et al., 2007]. Therefore, coagulation-flocculation must be followed by other treatment techniques. Moreover, this method consumes chemicals and thus produces large volume of sludge [Fenglian et al, 2011].

1.5.5. Adsorption

Adsorption is a mass transfer process by which a substance is transferred from the liquid phase to the surface of a solid, and becomes bound by physical and/or chemical interactions. The substance that accumulates at the interface is called adsorbate and the solid on which adsorption occurs is adsorbent [Dabrowski, 2001] Adsorption process can be of two types: chemical adsorption and physical adsorption Chemical adsorption or chemisorption is illustrated by the formation of strong chemical associations between molecules or ions of adsorbate to the functional group present on adsorbent surface, [Allen et al., 2005] and thus chemical adsorption is generally irreversible. Fig 1.4 illustrates how adsorbate molecule gets adsorbed on the surface of adsorbent. Physical adsorption or physisorption is characterised by weak van der Waals intraparticle bonds between adsorbate and adsorbent and thus reversible in most cases [Allen et al., 2005]. Adsorption phenomenon on most of the adsorbent including agricultural by-products is controlled by physical forces with some exception of chemisorption. In case of physical adsorption the main physical

forces controlling adsorption are van der Waals forces, hydrogen bonds, polarity, dipole–dipole interaction, etc. [Ali et al., 2010].

Activated carbon is one of the most widely used conventional adsorbent because of high surface area, micro porous structure, high adsorption capacity and high degree of surface reactivity. However, its widespread use in wastewater treatment is sometimes restricted due to its higher cost and poor regeneration capacity [Robinson, 2001]. These drawbacks of activated carbon have prompted a considerable research work in the search of inexpensive adsorbents especially developed from various agricultural waste materials. Therefore to make adsorption an economically feasible process, non-conventional adsorbents have come into application. During the last decades various non-conventional adsorbents have been used for the removal of heavy metals from wastewater such as rice husk [Elham et al., 2010; Singha 2012], wheat straw [Ajmal et al., 2003], wheat shell, almond shell [dang et al., 2009], hazelnut [Demirbasa et al., 2004], orange peel [Kobya et al., 2004], coffee waste [Ajmal et al., 2000], sugarcane bagasse [Martín-Lara et al., 2010] etc.

This process provides an attractive alternative for the treatment of polluted waters, especially if the sorbent is inexpensive and does not require an additional pretreatment step before its application [Dabrowski, 2001]. As for environmental remediation purpose, adsorption techniques are widely used to remove certain classes of chemical contaminants from waters, especially those that are practically unaffected by conventional biological wastewater treatments [Dabrowski, 2001, Allen et al., 2005]. Adsorption has been found to be superior to other techniques in terms of flexibility and simplicity of design, initial cost, insensitivity to toxic pollutants and ease of operation. Adsorption also does not produce harmful substances [Crini et al., 2006]. Various advantages and disadvantages related to the heavy metal removal techniques discussed above is summarized in Table 1.4.

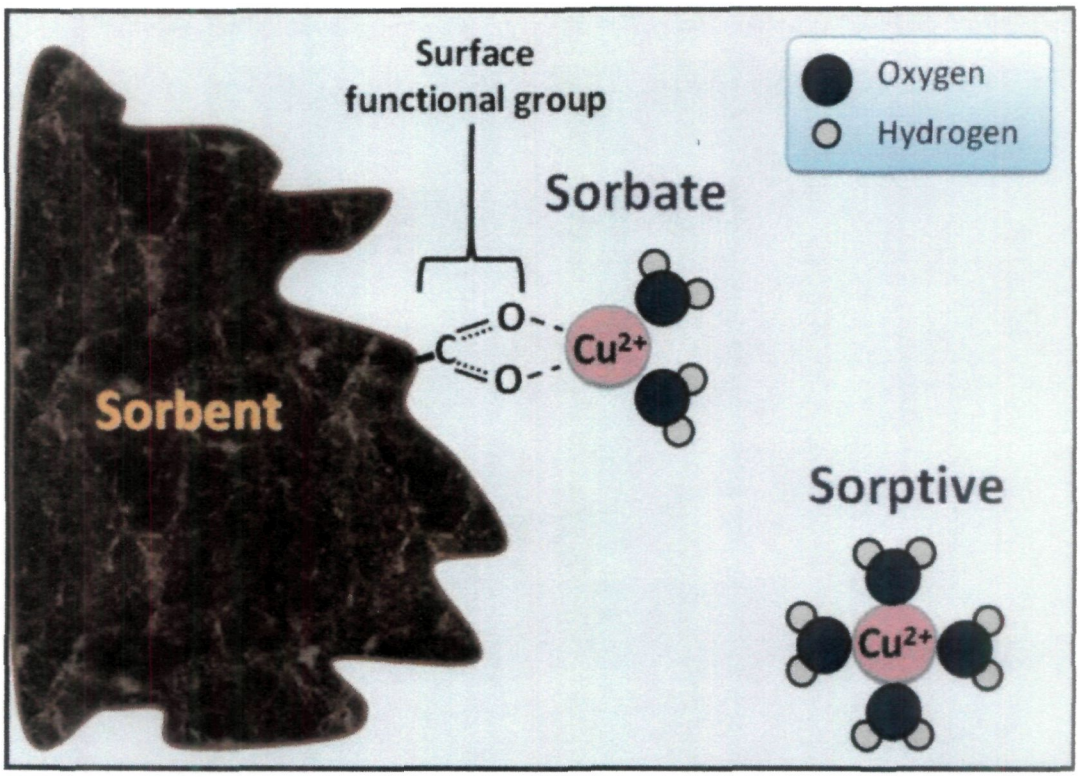


Fig 1.4: Chemical association between adsorbate and adsorbent during adsorption process [source: google images]

Table 1.4: Advantages and disadvantages of various treatment technologies for heavy metal removal

Technology	Advantages	Disadvantages	References
Chemical precipitation	Process simplicity Not metal selective Inexpensive capital cost	Large amount of sludge containing metals Sludge disposal cost High maintenance cost	Fenglian et al, 2011
Ion exchange	Metal selective *Limited pH* tolerance High regeneration	High initial capital cost High maintenance cost	*Rengaraj* et al., 2003
Membrane filtration	Low solid waste generation Low chemical consumption	Complex process High initial capital cost High maintenance and operation costs Membrane fouling Limited flow rates	Madaeni et al., 2003; Qin et al., 2008
Coagulation and flocculation	Bacterial inactivation capability Good sludge settling and dewatering characteristics	Chemical consumption Increased sludge volume generation	Fenglian et al, 2011

Adsorption	Wide variety of target pollutants High capacity Fast kinetics Efficient in removing metal ions even at ultra trace level Cost effective Process simplicity Possibly selective depending on adsorbent	Performance depends on type of adsorbent Physical or chemical activation to improve its sorption capacity.	Crini, 2005

1.5.5.1. Factors affecting adsorption of metal ions

There are many factors affecting metal adsorption such as solution pH, temperature, and initial metal ion concentration, adsorbent surface area, adsorbent particle size etc. Thus, the effects of these parameters are to be taken into account. Optimization of such conditions will greatly help in the development of industrial-scale metal removal treatment process. Some of the factors affecting adsorption of metals are listed in Table 1.5.

Table 1.5: Factors affecting adsorption of metal ions

Factors	Effects
Surface area of the adsorbent	Larger surface area implies greater adsorption capacity.
Particle size of the adsorbent	Smaller the particle size of the adsorbent greater is the adsorption capacity.
Contact time or Equilibrium time	Adsorption increases with increase in time until the attainment of equilibrium.
Concentration	Rate of adsorption increases with increase in concentration.
pH	Strong influence on adsorption due to the variation in degree of ionisation of metal ion in the solution and the surface properties of adsorbent [Nandi et el., 2009].
Temperature	Affects the rate and capacity of the adsorption [Argun et al., 2008].
Degree of ionization of the adsorbate molecules	Highly ionized molecules are adsorbed to smaller degree than neutral molecule.

1.6. TYPES OF ADSORBENTS

1.6.1. Activated Carbon

Activated carbon prepared from different source materials (e.g. coal, coconut shells, lignite, wood, etc.) is the most popular and widely used adsorbent in wastewater treatment throughout the world. Its application in the form of carbonized wood (charcoal) has been described first in the Sanskrit medical lore and then in the Egyptian papyrus. Sanskrit writings, dating about 2,000 BC, tell how to purify impure water by boiling it in copper vessels, exposure to sunlight, and filtering through charcoal [Gupta et al., 2009]. Activated carbon is produced by a process consisting of pyrolysis of raw material followed by activation with oxidizing gases. The product obtained is known as activated carbon and generally has a very porous structure with a large surface area ranging from 600 to 2,000 $m^2.g^{-1}$ [Grassi et al., 2012]. The high adsorptive capacities of activated carbons are mainly associated with their internal pore properties such as pore surface area, pore volume, and pore size distribution [Kadervelu et al., 2003]. Generally, activated carbons are mainly microporous, but in addition to micropores they contain meso and macropores (Fig 1.5), which are very important in facilitating access of the adsorbate molecules to the interior of the carbon particle [Bansal et al., 2005].

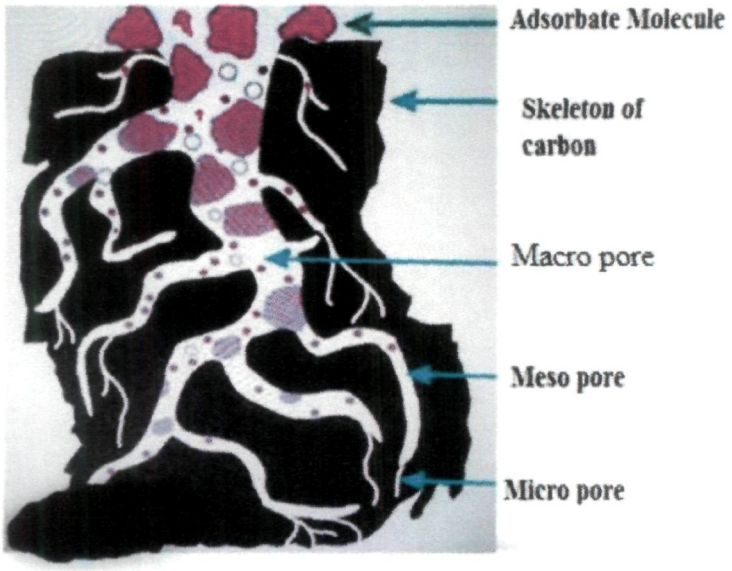


Fig 1.5: Different pores of activated carbon [source: google images]

1.6.2. Clays

Natural clay minerals are well known from the earliest day of civilization. Because of their low cost, high surface area, high porosity, and abundance in most continents, clays are good candidates as adsorbents. There are many kinds of clay: smectites (montmorillonite, saponite), mica (illite), kaolinite, serpentine, pylophyllite (talc), vermiculite, sepiolite, bentonite, kaolinite, diatomite, and Fuller's earth (attapulgite and montmorillonite varieties) [Gupta et al., 2009]. The adsorption capacities depend on negative charge on the surface, which gives clay the capability to adsorb positively charged species.

1.6.3. Minerals

Another class of adsorbents includes natural minerals. Among these, zeolite and goethite have been investigated in the adsorption of pharmaceuticals. Zeolite is typically used for the removal of dyes and heavy metals. Like clay minerals, adsorption capacity is linked to negative charge on the structure [Grassi et al., 2012].

1.6.4. Low Cost Adsorbents

Although, activated carbon is undoubtedly considered as universal adsorbent for the removal of diverse kinds of pollutants from water, its widespread use is sometimes restricted due to the high costs [Ahmaruzzaman, 2008; Grassi et al., 2012]. Attempts have been made to develop low-cost alternative adsorbents which may be classified in two ways either (i) on basis of their availability, i.e., (a) natural materials (wood, peat, coal, lignite etc.), (b) industrial/agricultural/domestic wastes or by-products (slag, sludge, fly ash, bagasse flyash, red mud etc.), and (c) synthesized products; or (ii) depending on their nature, i.e., (a) inorganic and (b) organic material [Grassi et al., 2012].

1.6.4.1. Agricultural Wastes

The basic components of the agricultural waste materials include hemicelluloses, lignin, lipids, proteins, simple sugars, water, hydrocarbons, and starch, containing a variety of functional groups [Bhatnagar, 2010]. In particular agricultural materials containing cellulose show a potential adsorption capacity for various pollutants. If these wastes could be used as low-cost adsorbents, it will

provide a two-fold advantage. Firstly, the volume of waste materials could be partly reduced and secondly the low-cost adsorbent, if developed, can reduce the treatment of wastewaters at a reasonable cost [Bhatnagar aet al., 2005; jain et al., 2003]. Agricultural waste is a rich source for activated carbon production due to its low ash content and reasonable hardness. The agricultural solid wastes from cheap and readily available resources such as almond shell, hazelnut shell [Demirbasa et al., 2004], poplar, walnut sawdust [Aydin et al., 2004], orange peel [**Kobya et al., 2004**], sawdust [shukhla et al., 2002], rice husk [[Elham et al., 2010; Singha 2012]], sugarcane bagasse [[Martín-Lara et al., 2010]], coconut burch waste [Hameed et al., 2008], and papaya seed [Hameed et al., 2009] have been investigated for the removal of pollutants from aqueous solutions.

The agricultural waste materials have been used in their natural form or after some physical or chemical modification. Pretreatment methods using different kinds of modifying agents such as base solutions (sodium hydroxide, calcium hydroxide, sodium carbonate) mineral and organic acid solutions (hydrochloric acid, nitric acid, sulfuric acid, tartaric acid, citric acid), organic compounds (ethylenediamine, formaldehyde, epichlorohydrin, methanol), oxidizing agent (hydrogen peroxide), and dyes for the purpose of removing soluble organic compounds, color and metal from the aqueous solutions have been performed.

1.6.4.2. Industrial Wastes

Widespread industrial activities generate huge amount of solid waste materials as by-products. Industrial wastes such as sludge, fly ash, and red mud are classified as low-cost materials, locally available and can be used as adsorbents for removal of pollutant from aqueous solution [Gulnaz et al., 2004].

Fly ash is a waste material originating in combustion processes. Although it may contain some hazardous substances, such as heavy metals, it has been showing good adsorption qualities for phenolic compounds. The maximum phenol adsorption capacity has been found to be 27.9 $mg.g^{-1}$ for fly ash and 108.0 $mg.g^{-1}$ for granular activated carbon at initial phenol concentration of 100 $mg.L^{-1}$ [Grassi et al., 2012].

Red mud is a waste material formed during the production of alumina [Mohan et al, 2007]. Red mud has been explored as an alternate adsorbent for arsenic. An alkaline aqueous medium (pH 9.5) favored As(III) removal, whereas the acidic pH range (1.1–3.2) was effective for As(V) removal [Altundogan et al., 2000; Altundogan et al., 2002].

1.7. SURVEY OF LITERATURE

Adsorption is considered an effective, efficient and economic method for the removal of pollutants from wastewater [Feng et al., 2010; Gupta & Nayak, 2012]. This technique can be applied frequently on large scale, as it can handle fairly large flow rates, producing a high quality of water without producing notorious sludge, residual contaminants, etc. [Gupta et al., 2007b; Gupta et al., 2011]. Moreover, adsorption is universal and fast in nature and applicable for the removal of organic and inorganic pollutants even at low concentration. Various kind of conventional and non-conventional adsorbents have been used for the removal of heavy metals. Recent literature survey on the adsorbent used for the removal of heavy metals form aqueous solution and wastewater are listed here.

Table 1.6: Summary of various adsorbents used for the removal of inorganic pollutants from water and wastewater (2008-2014)

Adsorbent	Heavy metals	Remarks	Reference
Black carrot residue	Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}	Best fitted by Langmuir isotherm, endothermic at high temperature.	Guzel et al., 2008
Modified pine bark	Cd^{2+}	Modified by Fenton reagent. Adsorption at pH 7, with 97 % removal.	Argun et al., 2008
Sphagnum peat	Pb^{2+}, Cu^{2+}, Ni^{2+}, Cd^{2+}, Zn^{2+}	Best fitted by pseudo second order kinetic and Freundlich isotherm.	Kalmykova et al., 2008
Sugarcane bagasse and mercerized sugarcane bagasse chemically modified with succinic anhydride(MMSCB)	Cu^{2+},Cd^{2+} and Pb^{2+}	Best fitted by Langmuir isotherm.	Gurgel et al., 2008
Grape stalk and coffee wastes	Cu^{2+} and Ni^{2+}	During desorption recovered more than 97% with 0.05 M HCl in presence of EDTA.	Escudero et al., 2008
Zeolitic MCM-22 and activated carbon	Pb^{2+}, Cu^{2+} and humic acid	Adsorption carried out in Single and binarysystem.	Terdkiatburana et al., 2008
***Ulmus carpinifolia* and *Fraxinus excelsior* tree leaves**	Pb^{2+}, Cu^{2+} and Cd^{2+}	Desorbed and regenerated by 0.2M HCl.	Sangi et al., 2008

Phosphate treated rice husk.	Pb^{2+}, Cu^{2+}, Zn^{2+} and Mn^{2+}	Fixed and column study for normal and treated adsorbent.	Mohan et al., 2008
Chemically modified plant wastes	Cd^{2+}, Cu^{2+}, Pb^{2+}, Ni^{2+}, Zn^{2+}	Modified by organic and mineral acids.	Nagah et al., 2008
Functionalized sepiolite	Co^{2+}, Cd^{2+}, Zn^{2+}, Mn^{2+}, Fe^{3+}	Surface modification of sepiolite with [3-(2-aminoethylamino) propyl] trimethoxysilaane.	Dogan et al., 2008
Makino bamboo charcoal	Pb^{2+},Cu^{2+},Cr^{3+} and Cd^{2+}	Bamboo charcoal activated by CO_2 at 800 °C had higher specific area as compared to bamboo charcoal activated by steam at 900 °C. The Charcoal activated by CO_2 shows higher % of adsorption capacity.	Wang et al., 2008
Fly ash	Pb^{2+}, Cu^{2+} and humic acid	Maximum adsorption capacity achieved at pH 5 and 30 °C.	Wang et al., 2008
Chestnut shell	Pb^{2+}, Cu^{2+}, and Zn^{2+}	Treatment of chestnut shell by formaldehyde.	Vazquez et al., 2009
Vermucilite clay minerals	Cr^{3+}, Cu^{2+}, Ni^{2+}, Co^{2+}	The ionic strength of adsorbent was studied using NH_4Cl, KCl and NaCl.	El-Bayaa et al., 2009
Mercerized cellulose and mercerized sugarcane bagasse chemically modified with EDTA dianhydride (EDTAD)	Cu^{2+},Cd^{2+} and Pb^{2+}	Cellulose and sugarcane bagasse were first modified by 5 $mol.L^{-1}$ NaOH and then by EDTA di anhydride. EDTAD treated material shows higher adsorption capacity.	Junior et al., 2009
Lignite and lignite washing plant tailing	Pb^{2+}	Adsorption at pH 9, equilibrium in 120 min for 300 ppm concentration.	Ucurum. 2009
Coal fly ash	Zn^{2+} Cu^{2+}, Ni^{2+}, Pb^{2+} and Cd^{2+}	Higher adsorption efficiency was achieved for Pb^{2+}.	Mohan et al., 2009
Zeolite synthesized from fly ash	Cu^{2+} and Zn^{2+}	Synthesized by hydrothermal treatment. Followed adsorption and ion exchange process.	Wang et al., 2009
Tunisian olive-waste cakes activated carbon	Cu^{2+}	Phosphoric acid as a precursor agent. Adsorption capacity enhanced by $KMnO_4$ carbon treatment.	Baccar et al., 2009
Sawdust of	Cu^{2+}	Equilibrium reached in 20 min. Maximum adsorption capacity at	Bozic et al.,

deciduous trees		pH 3.5-5.0.	2009
Chitosan and derivatives	Cu^{2+},Cd^{2+},Ni^{2+},Pb^{2+}		Wu et al., 2010
Polyacronitrile fiber	Cu^{2+}, Pb^{2+}		Zaini et al., 2010
Chemically modified sugarcane bagasse	Pb^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}	Sugarcane bagasse was modified by xanthalate. Equilibrium in 20-40 min.	Homagai et al., 2010
Date pits solid adsorbent	Cu^{2+}, Cd^{2+}	Followed both Langmuir and Freundlich model.	Ghouti et al., 2010
Orange peel xanthate	Cu^{2+},Cd^{2+},Ni^{2+},Pb^{2+},Zn^{2+}	Equilibrium reached in 20 min. Best fitted by Langmuir model and pseudo second order kinetics.	Liang et al., 2010
Fly ash	Dyes and heavy metals		Visa et al., 2010
Activated carbon of apricot stones	Pb^{2+},Cu^{2+},Cd^{2+},Zn^{2+}	Closed circuit of fluidized bed used. A homogenous solid diffusion model explains the mass transfer system.	Tsibranska et al., 2010
Poly(amidoxime)/SiO_2	Cu^{2+},Ni^{2+},Pb^{2+},Cd^{2+}		Gao et al., 2010
Arthrospira (Spirulina) platensis* and *Chlorella vulgaris	Ni^{2+}, Zn^{2+}, Pb^{2+}	Maximum adsorption at pH 5.0-5.5. C. vulgaris behaved as a better biosorbent. (qe = 0.495, 0.634 and 0.664 mmol g^{-1}, respectively).	Ferreira et al., 2011
Novel biopolymer coated hydroxyapatite	Pb^{2+}, Cu^{2+}, Cd^{2+}		Vila et al., 2011
Chemically modified orange peel	Pb^{2+}, Cd^{2+}, Zn^{2+}	Desorbed by 0.01M HCl.	Feng et al., 2011
Dairy manure compost	Pb^{2+}, Cu^{2+}, Zn^{2+}		Zhang, 2011
Supercritical CO_2 on banana peels	Cu^{2+}	Best fitted by Langmuir and Freundlich isotherm.	Albarelli et al., 2011
Industrial wastes as low cost adsorbent	Heavy metals		Ahmaruzzaman, 2011
Cryogels containing iminodiazole groups	Pb^{2+}, Cd^{2+}, Zn^{2+}, Cu^{2+}	Maximum adsorption capacity was achieved for Pb^{2+}.	Tekin et al., 2011
Peanut shell	$Cr^{3+}$and Cu^{2+}	Best fitted by Langmuir isotherm.	Krowiak et al., 2011

Chitosan	Cu^{2+}, Hg^{2+}, Pb^{2+}, Zn^{2+}	Produced from the shrimp shell. Best fitted by Langmuir isotherm.	Zubiate et al., 2011
Magnetically recoverable facile nanomaterials	Pb^{2+}	Average diameter of adsorbent is 60 nm. Regeneration by 0.1M HCl.	Zhang et al., 2011
Monto-morillonite and calcareous clays.	Pb^{2+}, Cd^{2+} ,Cu^{2+},Zn^{2+}	Surface area of adsorbent was found to be less than 71 $m^2.g^{-1}$.	Sdiri et al., 2011
NH_2 grafting on mesoporous SBA-15 surface.	Cu^{2+} ,Cd^{2+}, Zn^{2+} ,Cr^{3+}, Ni^{2+}	Utilizing the reaction between toluene diisocyanate (TDI), silanol and ethylenediamine (EDA).	Zhao et al., 2011
Salicylic acid type chelate adsorbent	Cu^{2+}, Cd^{2+}, Zn^{2+}, Pb^{2+}	5-aminosalicylic acid was grafted with poly (glycidyl-methacrylate).Best fitted by Langmuir and Freundlich isotherm. High regeneration capacity with 0.1M HCl.	An et al., 2011
Electrospum membrane of cellulose acetate	Cu^{2+}, Cd^{2+} and Hg^{2+}	The adsorption capacity was dependant on pH. High adsorption selectivity for Hg^{2+}	Tian et al., 2011
***Ulva lactuca* algae**	Ni^{2+}, Cu^{2+}, Cd^{2+}, Pb^{2+}	Followed intraparticle diffusion model.	Zakhama et al., 2011
Fungal species *P.ostreatus*	Cu^{2+}, Ni^{2+}, Zn^{2+}, Cr^{2+}	High regeneration ability, maximum adsorption of Cr^{6+} at pH 2.5 whereas for Ni, Cu, Zn at pH 4.5-5.0.	Javaid et al., 2011
Peanut husk incinerated residues	Pb^{2+}, Zn^{2+}, Cd^{2+} and Ni^{2+}		Taha et al., 2011
EDTA modified chitosan-silica hybrid materials	Co^{2+}, Cd^{2+}, Ni^{2+}, Pb^{2+}.	Best fitted by pore diffusion model and Langmuir isotherm. High adsorption capacity for Pb^{2+}	Repo et al., 2011
Local landfill clay	Cr^{3+} and Cd^{2+}		Ghorbel-Abid et al., 2011
Chitosan composites	Heavy metals and dyes	Various form of chitosan composites used.	Wan Nagah et al., 2011
Mustard oil cake	Ni^{2+}	Maximum adsorption at pH 8. Follow Temkin model at 30°C and 40°C and Freundlich model at 50°c. Regeneration quite successful in acidic medium.	Khan et al., 2012
Potamogeton pusillu	Cu^{2+} and Cr^{6+}	An aquatic macrophyte. Removal done under 15 days of	Monferran et al., 2012

		phytoextraction experiment.	
Orange peel and Fe_2O_3 nanoparticles	Cd^{2+}		Gupta et al., 2012
Kolubara lignite	Cu^{2+}	Equilibrium time 5 min, pH 5 with 90% removal.	Milicevic et al., 2012
Lactobacillus bulgaricus* and *Streptococcus thermophilus	Cu^{2+},Cd^{2+}, As^{3+}	Single and tertiary system (copper, chromium, arsenate) were used. Tertiary system was quite effective.	Chang et al., 2012
Mineral powder additive	Cu^{2+}, Cd^{2+}, Pb^{2+}, Ni^{2+}, Fe^{3+}	Vitrification process has been used with mineral powder additives to remove metal from electroplating sludge.	Cheng Chou et al., 2012
Municipal solid waste leacheate	Cd^{2+} and Cu^{2+}	.	Wu et al., 2012
Zinc oxide nanoparticles	Cr^{6+}	Prepared chemically from zinc acetate solution in proportion with 5% alcohol.	Banerjee et al., 2012
Natural limestones	Pb^{2+}, Cu^{2}+, Cd^{2+}, Zn^{2+}	Best fitted by pseudo second order kinetic and intra particle diffusion model.	Pellera et al., 2012
Green algae waste	Pb^{2+}, Cd^{2+}, Co^{2+}		Bulgariu et al., 2012
732 cation-exchange resin	Pb2+	Adsorption capacity of Pb^{2+} was 396.8 $mg.g^{-1}$ at pH 4..	Guo et al., 2013
microporous organo-birnessite	Pb^{2+}		Lee et al., 2013
Castor leaf [*Ricinus communis* L.] powder	Pb^{2+}, Cd^{2+}	Adsorption capacity of 0.094 and 0.05 $mmol.g^{-1}$ for Cd(II) and Pb(II) respectively, was observed	Martins et al., 2013
Magnetic modified sugarcane bagasse	Pb^{2+}, Cd^{2+}	Adsorption capacities for Pb^{2+} and Cd^{2+} were 1.2 and 1.1 mmol g^{-1}, respectively.	Yu et al., 2013
Crystalline mesoporous ZrO_2–Al_2O_3 hierarchical nanostructures	Pb^{2+}	maximum adsorption capacity was 110.49 $mg.g^{-1}$.	Tian et al., 2013
Hydrothermally treated municipal sludge & pulp	Pb^{2+}	Both ADS and INS were found to remove Pb(II) effectively and followed Sips adsorption	Alatalo et al., 2013

and paper industry sludge		isotherm.	
Bornean oil palm shell	Cu2+, Pb^{2+}	Monolayer adsorption capacities were found to be 1.756 and 3.390 $mg.g^{-1}$ for Cu(II) and Pb(II), respectively.	Chong et al., 2013
***Rosa bourbonia* phyto-biomass**	Cu2+, Pb^{2+}	.	Manzoor et al., 2013
Mesoporous activated carbons fabricated from water hyacinth using H_3PO_4activation	Pb^{2+}	The maximum monolayer capacity (qm) was found to be 118.8 $mg.g^{-1}$	Huang et al., 2014
Modified *Agaricus bisporus*	Pb^{2+}	Adsorption capacity of 86.4 mg g^{-1} was achieved after modification with NaOH	Long et al., 2014
Mesoporous cadmium phosphate	Pb^{2+}	Thermodynamic parameters ΔG, ΔH and ΔS were – 5.95 kJ mol^{-1}, 15.08 kJ mol^{-1}, and 68.09 J K^{-1} mol^{-1}, respectively	Yin et al., 2014
Silicon carbide nanoparticles	Pb^{2+}	The adsorption capacity was 156.2 mg g^{-1}.	Pourezza et al., 2014
Magnetic $CoFe_2O_4$-reduced graphene oxide	Hg^{2+}, Pb^{2+}	The adsorption capacity for Pb^{2+} was 299.4 $mg.g^{-1}$ at pH of 5.3 and 25 °C; while for Hg^{2+} was 157.9 $mg.g^{-1}$ at pH of 4.6 and 25 °C.	Zhang et al., 2014
Surface-imprinted activated carbon sorbent	Cu^{2+}	The maximum static adsorption capacity of the ion-imprinted and non-imprinted sorbent for Cu^{2+} was 26.71 and 6.86 $mg.g^{-1}$, respectively	Li et al., 2014

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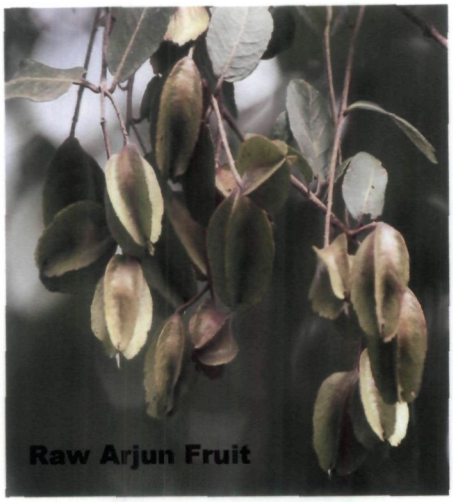

Raw Arjun Fruit


Ripe Arjun Fruit

CHAPTER -2

Adsorption Studies of Pb (II) on Arjun Tree Fruit (Terminalia arjuna)

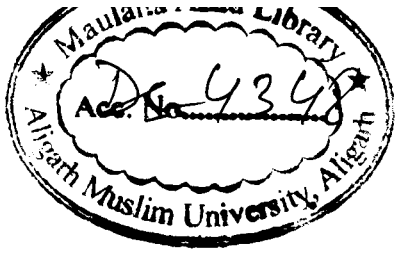
2.1. INTRODUCTION

Owing to the rapid industrialization and urbanization, environmental degradation is accelerating day by day due to the contaminants being released in air soil and water [Zhou et al., 2009]. The most significant pollutants found in wastewater are heavy metals. They are persistent in nature and highly toxic even at ultra trace levels [Ozdesa et al., 2009]. Since they are non-biodegradable they tend to accumulate in the tissues and vital organs of living organism thereby causing various diseases and long term disorders [Loutseti et al., 2009]. Among the variety of heavy metals found in wastewater Pb(II) is considered to be one of the most poisonous contaminant. This metal is known to cause a number of adverse effects on human health as it can accumulate in the kidney, liver, brain, bones, and muscles. Chronic toxicity occurs at blood levels of 0.4–0.6 $mg.L^{-1}$ [Flora et al., 2012]. The maximum permissible limit assigned by World Health Organization (WHO) for Pb(II) in drinking water is 0.05 $mg.L^{-1}$ [Rao et al., 2011]. As reported by health organizations, Pb(II) can alter numerous metabolic body processes and induce impairment and dysfunction in the blood and cardiovascular system in human adults and particularly in children [Moreira et al., 2001]. The condition of children in developing countries is quite miserable with more than 15 million of them are suffering from permanent neurological damage due to Pb(II) poisoning [HEI special report 15, 2004].

Keeping in mind the hazardous effects of Pb(II) it seems to be the need of hour to remove Pb(II) from water and wastewater. Some of the techniques commonly employed to remove Pb(II) from aqueous solutions include membrane filtration, ultra-filtration and reverse osmosis, chemical precipitation of Pb(II) as the hydroxide and sulfide and ion-exchange[Gzara et al., 2001; Chen et al., 2009; Kongsuwan et al., 2009; Deng et al., 2013; Galindo et al., 2013; Sarada et al., 2013]. All these methods suffer from one or the other drawback. Some of the drawbacks include high operational cost, production of a chemical byproduct that requires further treatment, low removal efficiency, difficult implementation etc. Adsorption is a quite attractive process for the removal of Pb(II) from aqueous solutions. Activated carbon has long been used as effective adsorbent but owing to its high cost and difficulty in regeneration some naturally occurring biomass or by-products obtained from agricultural or industrial processes are preferably used in adsorption process as they are available in abundance, economical, easily prepared and eco-friendly. The most

significant feature of this naturally occurring biomass is that they do not release any toxic or objectionable substance when added into water or wastewater for treatment. Various studies on Pb(II) removal from aqueous solution using natural adsorbents include activated carbon prepared from biomass materials [Goel et al., 2005], rice husks [Elham et al., 2010; Singha et al., 2012], tree fern [Ho et al., 2004], maize husks [Zvinowanda et al., 2010], sawdust [Ahmad et al., 2009; Ofomaja et al., 2010], sugarcane bagasse [Martín-Lara et al., 2010], coriander seed [Rao et al., 2012], NOC (neem oil cake) [Rao et al., 2007], modified water hyacinth [Nabila et al., 2014],castor leaf powder [Amanda et al., 2013], green alga [Sari et al., 2008], laminaria japonica [Ghimi et al., 2008] etc.

The objective of the present work is to explore the adsorption efficiency of *Terminalia arjuna* fruit for the removal of Pb(II) from aqueous solution. *Terminalia arjuna*, commonly known as arjuna or arjun belongs to the family combretaceae. It is a large evergreen tree and the height reaches upto 60-80 feet. It is mainly found in the greater parts of Indian peninsula along rivers and sub-Himalyan tract, chota nagpur, orissa, west Bengal, Punjab, deccan and konkan. Flowering begins in April and extends to May with the fruit ripening the following February-May, nearly a year after the appearance of the flowers. The diameter of fruit is 1-1.5 inch with 5-7 longitudinal lobes [Parakh, 2010]. *Terminalia arjuna* is a widely used medicinal plant. The bark of the plant is quite useful and finds its application in the treatment of heart diseases, diabetes, tumour, skin disorder, inflammation, asthma, etc [Parakh, 2010]. The bark, leaves and fruit possesses glycosides, large quantities of flavonoids, tannins and minerals [Nema et al., 2012]. Phenolic contents of these parts are also quite high (72.0–167.2 $mg.kg^{-1}$) [Bajpai et al., 2005]. In comparison to other commonly used medicinal plants, bark of *Terminalia arjuna* contains a very high level of flavonoids. Some of the flavonoids obtained from its bark include pelorgonidin, arjunolone, flavones, kempferol, quercetin, and bicalein [Nema et al., 2012]. The fruit of *Terminalia arjuna* is found to possess large number of phytochemicals namely: Arjunone, methyl oleanolate, gallic acid, hentriacontane, arachidic stearate, ellagic acid, arjunic acid, β-sitisterol, friedelin, myristil oleate [Parakh, 2010].



2.2. MATERIAL AND METHODS

2.2.1. Preparation of adsorbent

Terminalia arjuna nuts used in this study were collected locally from university campus of Aligarh, U.P., India in the month of May. Collected nuts were washed several times with distilled water in order to remove adhering dirt and dust particles and then dried in an open air oven at 60°C for 48 h. The dried sample was grounded and sieved through 0.300-0.150 mm screen size using standard ASTM sieves. The sieved sample was again washed repeatedly with double distilled water (DDW) until the wash water contained no colour. The biomass was finally dried at 60°C for 24 h in oven and was stored in an air tight bottle for further study.

2.2.2. Chemicals and reagents

All chemicals and reagents used were of analytical grade (A.R) and were obtained from Merck, Germany. They were used as such without further purification. Stock solution of Pb(II) (1000 $mg.L^{-1}$) was prepared by dissolving appropriate amount of lead nitrate salt in required volume of doubled distilled water (DDW). Working standard solutions of Pb(II) of desired concentrations were obtained by diluting the stock solution.

2.2.3. Characterization of adsorbent

To investigate the physical surface morphology of the adsorbent before and after Pb (II) adsorption, scanning electron microscopy (SEM) of gold coated samples were carried out on a carbon tape in a JSM-6510LV scanning electron microscope (JEOL, Japan) at an accelerating voltage of 20 kV and magnification of 7500. The type of binding groups present on the adsorbent were examined by Fourier transform infrared (FTIR) analysis with pellets prepared by mixing spectroscopic grade potassium bromide (KBr) and the adsorbent in the ratio of 4:1. The spectra were recorded in the range of 400–4000 wave number (cm^{-1}) in the diffuse reflectance mode at a resolution of 4 cm^{-1} in KBr pellets. The determination of elemental composition of the adsorbent before and after Pb(II) adsorption was carried out using the Oxford Instruments INCA X-sight energy dispersive X-ray (EDAX) spectrometer equipped SEM. The zero surface charge characteristic of the adsorbent was determined by solid addition method [Lataye et al., 2006].

2.2.4. Batch adsorbtion studies

The adsorption properties of TAFP were investigated as a function of adsorbent dose, initial pH, initial metal ion concentration, contact time and temperature. Thermodynamics and kinetics studies were carried out by batch process. 0.2 g of adsorbent was weighed and placed in a series of 250 mL standard conical flasks containing 20 mL of pb(II) solution of desired concentration. The mixture was then shaken in a temperature controlled incubator shaker for different contact times (5 min to 24 h). The conical flasks were taken out from shaker at a predetermined time interval and the mixture was filtered using whatmann filter paper No.1. The final concentration of Pb(II) in filtrate was then determined by atomic absorption spectrophotometer (AAS). The % adsorption of Pb(II) and the adsorption capacity, q_e ($mg.g^{-1}$) of the adsorbent at equilibrium were determined using the following relationships.

$$\% \text{ Adsorption} = \left(\frac{C_o - C_e}{C_o}\right) \text{x } 100 \qquad (1)$$

$$\text{Adsorption capacity}, q_e = \left(\frac{C_o - C_e}{W}\right) \text{x V} \qquad (2)$$

Where, C_o & C_e are the initial and final Pb(II) concentration respectively; V is the volume of the solution (L) and W is the mass of the adsorbent (g).

2.2.4.1. Effect of contact time

A series of 250 mL conical flasks, each containing 0.2 g adsorbent and 20 mL solution of Pb(II) of concentration 50 $mg.L^{-1}$, were shaken in a temperature controlled incubator shaker. The flasks were taken out from shaker at a predetermined time interval and were filtered using whatmann filter paper No.1. The concentration of Pb(II) in each filtrate was then determined by AAS and the amount of Pb(II) adsorbed in each case was determined as described above.

2.2.4.2. Effect of pH

The effect of pH was studied in the pH range of 1–10. The experiments were carried out in batch mode as follows: 40 mL of Pb(II) solution of concentration 50

$mg.L^{-1}$ was taken in a beaker. The pH adjustment of solution was done by adding either 0.1N HNO_3 or 0.1N NaOH. The concentration of Pb(II) in this solution was then determined (initial concentration). 20 mL of this solution was taken in conical flask and treated with 0.2 g adsorbent. The mixture was shaken in a shaker incubator at the speed of 110 rpm. After equilibrium, the mixture was filtered and the final concentration of Pb(II) in filtrate was determined by AAS. The final or equilibrium pH (pH_f) was also recorded by using pH-meter. In order to investigate the effect of electrolyte (KNO_3), same procedure was followed as described above except that Pb(II) solution of 50 $mg.L^{-1}$ concentration was prepared in 0.1N KNO_3 solution instead of DDW

2.2.4.3. Point of zero charge (PZC)

The zero surface charge characteristics of the adsorbent were determined by solid addition method [Lataye et al., 2006]. The experiment was carried out as follows: 15 mL of 0.1 N KNO_3 solution was placed in each of a series of 100 mL conical flasks. The initial pHs (pH_i) of the solutions were roughly adjusted between 1 to 10 by adding either 0.1 N HNO_3 or 0.1 N NaOH solutions. The total volume of the solution in each flask was made upto 20 mL by adding KNO_3 solution of the same strength. The initial pH values (pH_i) of the solutions were accurately measured by using pH-meter. Thereafter 0.2 g of adsorbent was transferred into each flask and the mixture was allowed to equilibrate for 24 h with intermittent manual shaking. After equilibrium, solutions were filtered and the final pH (pH_f) of the supernatant liquid was recorded. The point of zero charge curves was obtained by plotting difference between the initial pH (pH_i) and final pH (pH_f) i.e. ΔpH values against pH_i. The point of intersection of the resulting curve with the abscissa, at which $\Delta pH = 0$, gave the pH_{PZC} value.

2.2.4.4. Effect of adsorbent dose

To study the effect of adsorbent dose on the adsorption of Pb(II), a series of 250 mL conical flasks each containing a fixed volume of Pb(II) solution (20 mL) of known concentration (50 $mg.L^{-1}$) were treated at 30°C with varying amount of adsorbent (0.1–1.0 g). The flasks were kept in a shaker incubator and shaken at the speed of 110 rpm the solutions were then filtered after 24 h. The amount of Pb(II) in the filtrate was then determined by AAS.

2.2.5. Breakthrough studies

0.5 g of adsorbent was accurately weighed and transferred into a glass column (0.6 cm internal diameter) with glass wool support. 250 mL of Pb(II) solution with initial concentration (C_0) of 50 $mg.L^{-1}$ was then passed through the column with a flow rate of 1 $mL.min^{-1}$. First 100 mL of the effluent was collected in 10 mL fractions and the remaining volume was collected in 50 mL fractions. The amount of Pb(II) (C_e) in each fraction was then determined by AAS. The breakthrough curve was obtained by plotting C_e/C_0 versus volume of the effluent.

2.2.6. Desorption studies

The exhausted column obtained after the determination of breakthrough capacity was used to study the desorption behaviour. The column was washed several times with DDW in order to remove traces of Pb(II) ions remained unadsorbed. 0.1N HCl was used as desorbing solution for the desorption of Pb(II) ions from adsorbent. The solution was passed through the column at a flow rate of 1 $mL.min^{-1}$ and the effluent was collected in 10 mL fractions. Each fraction was then analyzed by AAS for determining the amount of Pb(II) desorbed.

2.3. RESULTS AND DISCUSSIONS

The adsorption efficiency of *Terminalia arjuna* fruit powder (TAFP) for various heavy metal ions was investigated and it was observed that the adsorbent showed highest affinity towards Pb(II) followed by Zn(II), Ni(II), Cd(II), Cr(VI) and Cu(II) (Fig. 2.1). The monolayer adsorption capacity of Pb(II) investigated in the present study is higher than many other non conventional adsorbents reported earlier as summarized in Table 2.1.

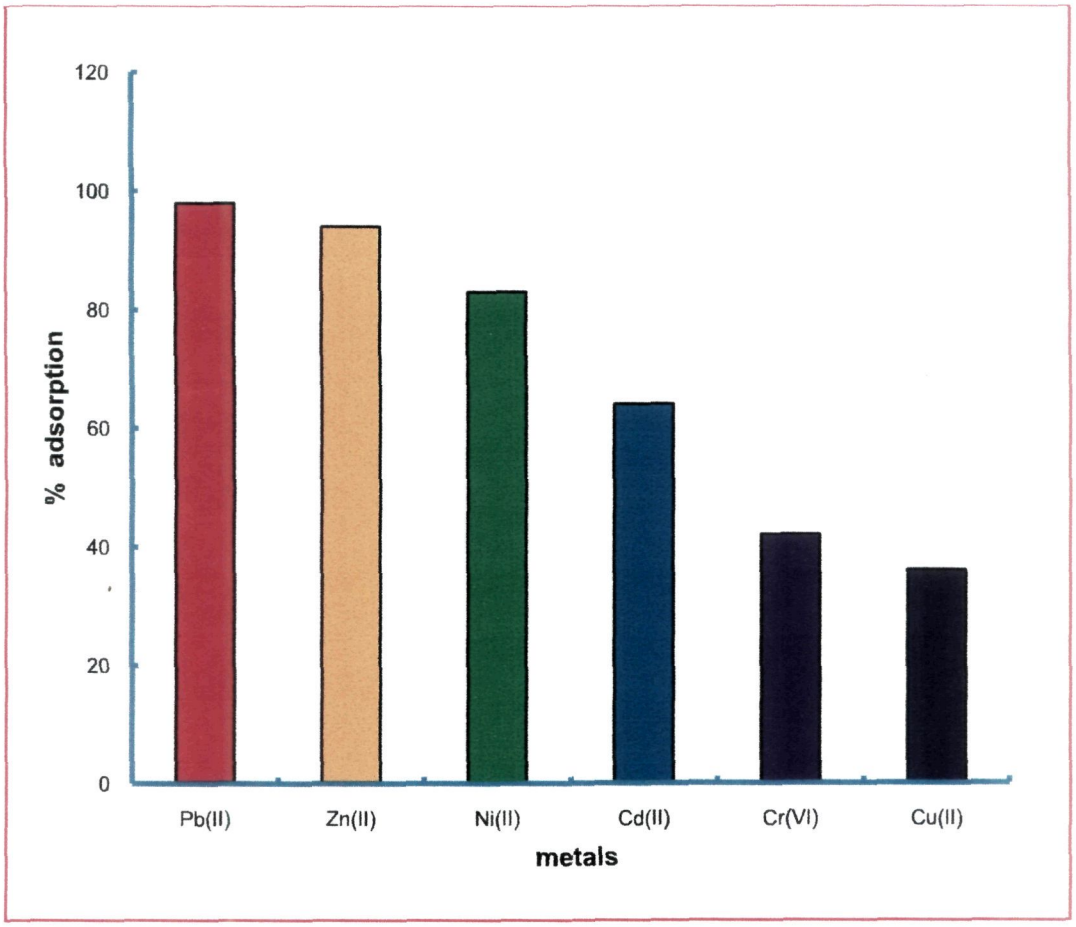


Fig 2.1: Percent adsorption of heavy metal ions from aqueous solution onto TAFP (Conditions; adsorbent dose = 0.2 g, temperature = 30° C)

Table 2.1: Comparison of the adsorption capacity of various adsorbents towards Pb(II) ions as reported in literature

Adsorbents	Adsorption capacity ($mg.g^{-1}$)	References
Ball clay	03.52	Rao et al., 2011b
Barley straw	23.20	Ho et al., 2004
Coir	18.90	Conrad et al., 2007
Chemically modified oil palm fruit fibre	05.58	Abia et al., 2008
Coral	01.14	Ahmad et al., 2012
Egg shell	04.74	Ahmad et al., 2012
Hazelnut shells	16.23	Iqbal et al., 2009
Imperata cylindrica leaf powder	13.50	Hanafiah et al., 2006
Oil palm shell	03.39	Chong et al., 2013
Olive cake	19.53	Iqbal et al., 2009
Orange peels	01.22	Xuan et al., 2006
Pinus sylvestris	09.71	Ghasemi et al., 2014
Rice husk	11.40	Iqbal et al., 2009
***Terminalia arjuna* fruit powder**	**27.39**	**Present study**

2.3.1. Characterization of adsorbent

2.3.1.1. Scanning electron microscope (SEM) analysis

SEM was carried out to examine the surface morphology of TAFP before and after adsorption of Pb(II). Scanning electron micrographs are depicted in Fig. 2.2. In both the cases surface of the adsorbent appeared to be irregular and porous. The surface of adsorbent before adsorption of Pb(II) seems to be less dense while after adsorption it became denser, showing adherence of Pb(II) on the surface .

2.3.1.2. EDX analysis

EDX spectra of TAFP before and after adsorption of Pb(II) are illustrated in Fig. 2.3. Spectra before adsorption clearly indicated the peak for the presence of carbon and oxygen as major constituents. EDX spectra after adsorption showed a peak due to Pb(II). The weight % of different constituents obtained from EDX analysis before and after Pb(II) adsorption are reported in Table 2.2. Moreover, before and after adsorption no characteristic peaks were observed for any impurities.

Table 2.2: EDX analysis

Elements	Before adsorption		After adsorption	
	Weight%	**Atomic%**	**Weight%**	**Atomic%**
C	45.46	52.61	44.60	52.06
O	54.54	47.39	54.64	47.88
Pb	-	-	0.76	0.05
Total	**100.00**	**100.00**	**100.00**	**100.00**

2.3.1.3. Fourier transform infrared (FTIR) spectroscopy

FT-IR analysis was carried out to identify characteristic functional groups present in TAFP and the spectra of the adsorbent before and after adsorption of Pb(II) are shown in Fig. 2.4 (a) and 2.4(b). The broad and strong absorption peak at 3446 cm^{-1} indicated the presence of OH group [Rao et al., 2011a]. The sharp and intense peak at 1642 cm^{-1} was aroused due to stretching vibrations of C=C [Haque et al., 2008], while the band at 1429 cm^{-1} indicated the presence of $-COO^-$ group [Rao et

al., 2011b]. The broad peak at 1122 cm^{-1} was due to C–O stretching vibrations [wang et al., 2013]. The broad and short peak observed at 601cm^{-1} might be due to M-O (metal-oxide) bond as metal oxides generally give absorption bands below 1000 cm^{-1} arising from inter-atomic vibrations [Anandan et al., 2011; wang et al., 2013]. FTIR spectra of the adsorbent after adsorption of Pb(II) (Fig. 2.4(b)) showed shift in some of the absorption bands towards lower frequencies. Shifting of bands to lower frequencies indicates bond weakening while a shift to higher frequencies indicates an increase in bond strength [Dwivedi et al., 2011; Wang et al., 2013]. Shifting of the peaks was observed in the region close to 1642 cm^{-1}, 1122cm^{-1} and 601 cm^{-1}. These peaks were shifted to 1629 cm^{-1}, 1068 cm^{-1} and 587 cm^{-1} respectively. The disappearance of peak at 1429 cm^{-1} indicated the strong interaction of Pb(II) with COO group.

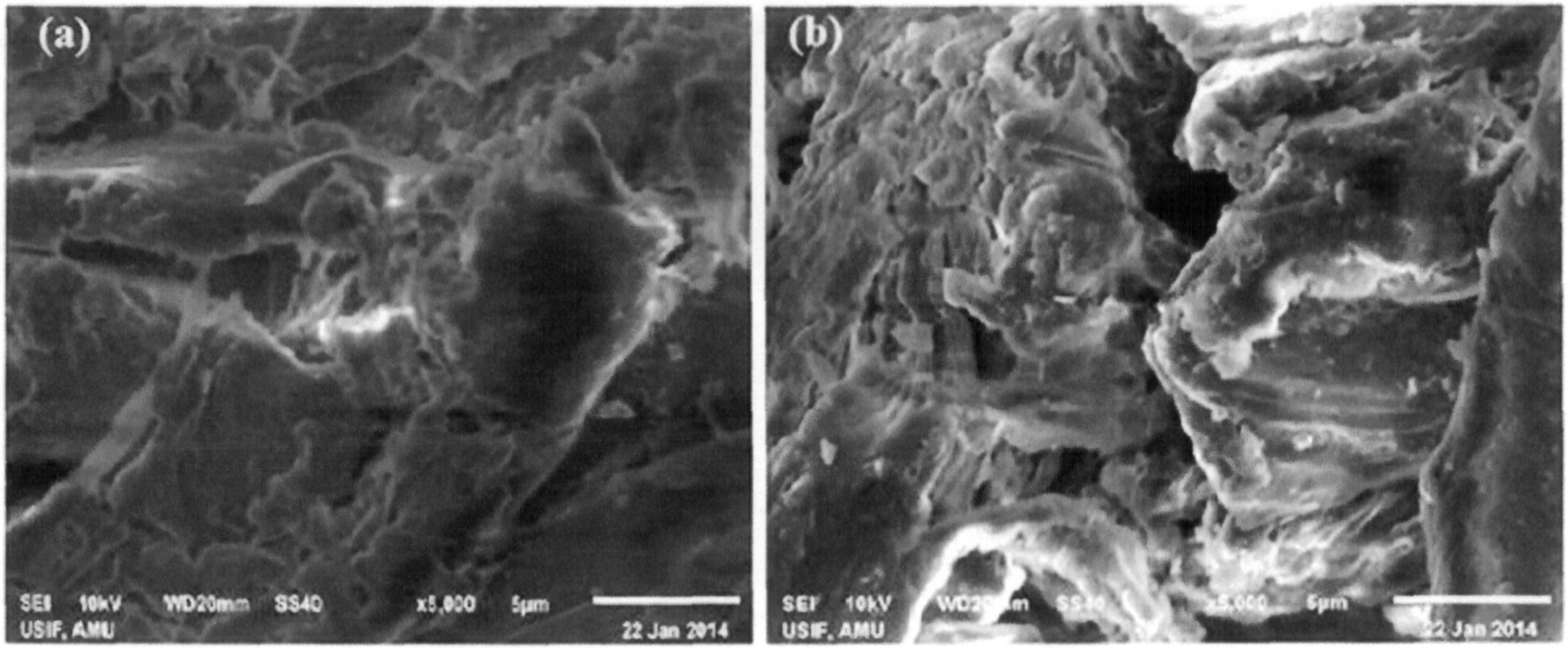


Fig 2.2: SEM micrograph of TAFP (a) before and (b) after adsorption of Pb(II) onto TAFP (Magnification: 5000 in both

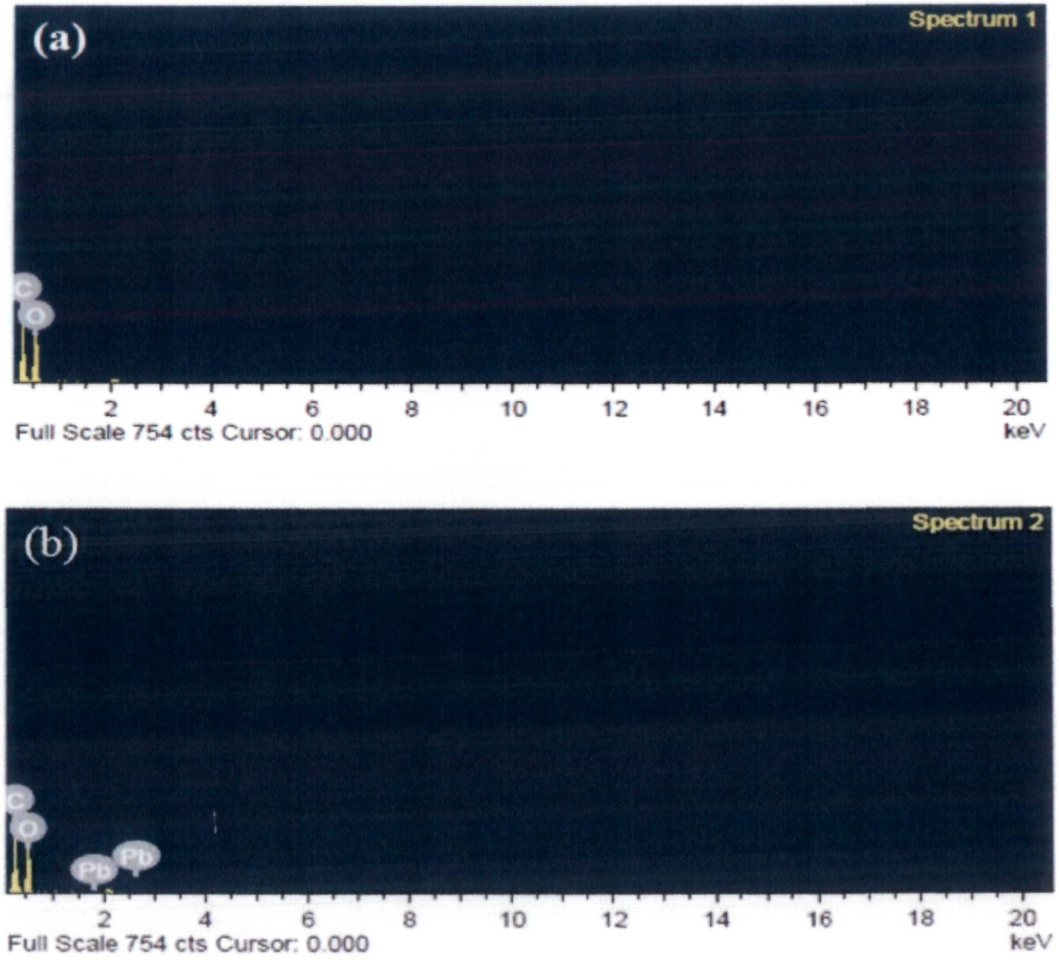


Fig 2.3: EDX spectra of TAFP (a) before and (b) after adsorption of Pb(II) onto TAFP

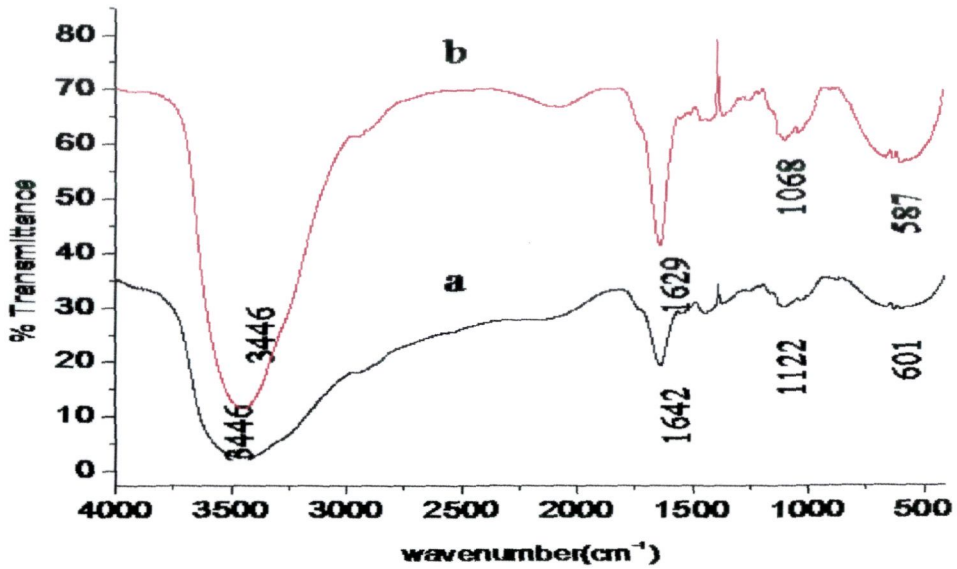


Fig 2.4: FTIR spectra of TAFP (a) before and (b) after adsorption of Pb(II) onto TAFP

2.3.2. Effect of initial Pb(II) concentration and contact time

The effect of initial concentration of Pb(II) onto adsorption was studied in the concentration range of 10-100 $mg.L^{-1}$(Fig. 2.5). A usual phenomenon of increase in adsorption capacity with increase in initial Pb(II) concentration was observed which may be attributed to the increased concentration gradient between the bulk solution and adsorbent surface thereby lowering the resistance to mass transfer of Pb(II) from aqueous to solid phase [Aksu et al., 2001; Rao et al., 2007]. The maximum adsorption of Pb(II) at equilibrium was found to be 0.95,1.92, 4.91, 5.90, 7.85, and 9.80 $mg.g^{-1}$ at initial Pb(II) concentrations of 10, 20, 50, 60, 80, and 100 $mg.g^{-1}$ respectively. The contact time required to reach equilibrium was found to be dependent on initial Pb(II) concentration up to 80 $mg.L^{-1}$ and then became independent of concentration (Fig. 2.5). This was due to the fact that empty adsorbent sites adsorbed Pb(II) ions rapidly at lower concentration but at higher concentration adsorption of Pb(II) ions occurred by diffusion (slower step) into the inner sites of the adsorbent. The equilibrium time of 5-30 min investigated in the present work is much shorter than many other adsorbents reported earlier for Pb(II) adsorption (Table 2.3).

Table 2.3: Comparison of equilibrium time for the adsorption of Pb(II) onto various adsorbents

Adsorbents	Equilibrium time (min)	Conc.(mg.L^{-1})	References
Coriander seed	60-120	50-70	Rao et al., 2012a
Green alga	60	10	Sari et al., 2008
Sugarcane bagasse	120	100	Hamza et al., 2013
Mentha piperita treated carbon	180	50	Ahmad et al., 2012
Penicillium oxalicum	120	100	Svecova et al., 2006
Spirodela polyrhiza(L)schleiden biomass	72	100	Meitei et al., 2013
***Terminalia arjuna* fruit powder**	**5-30**	**10-100**	**Present study**

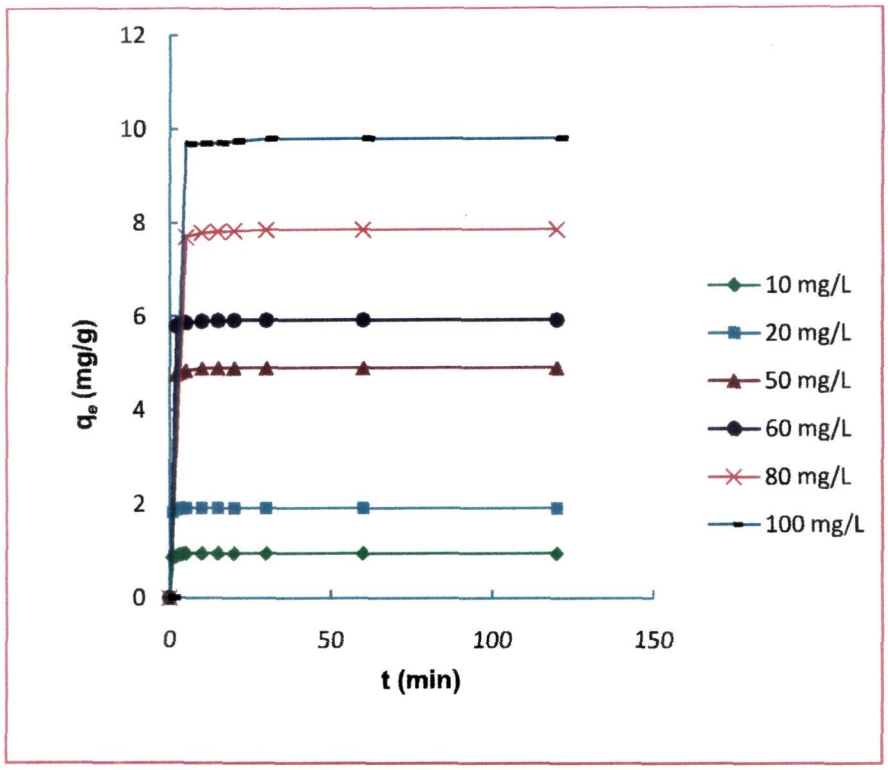


Fig 2.5: Effect of contact time on the adsorption of Pb(II) onto TAFP at different concentration (conditions; pH = 4; adsorbent = 0.2g; temp = 30°C)

2.3.3. Effect of pH

The effect of pH on the adsorption of Pb(II) was investigated in the pH range of 1–10. The results are shown in Fig. 2.6. The % adsorption of Pb(II) was minimum at pH 2 and increased with increasing pH, reached maximum (96%) at pH 4 but beyond pH 4 the % adsorption decreased slowly up to pH 10. The effect of pH on the adsorption of Pb(II) can be explained on the basis of the initial pH (pH_i) of the solution, final or equilibrium pH (pH_f), surface charge of the adsorbent and the speciation of the metal ions in the solution[Pourreza et al., 2014]. The adsorbent surface (MOH) would be completely covered by H^+ ions (MOH_2^+) at lower pH because of the presence of excess of H^+ ions but at higher pH hydroxide ions react with hydrous oxide to produce deprotonated oxide (MO^-) as shown in the following reactions [Inan et al., 2010; Kumar et al., 2013].

$$MOH + H^+ \rightarrow MOH_2^+ \quad (3)$$

$$MOH + H^- \rightarrow MO^- + H_2O \quad (4)$$

$$MOH^{+2} + 2OH^- \rightarrow MO^- \quad (5)$$

Therefore the adsorbent surface became positively charged at lower pH and negatively charged at higher pH. Fig. 2.6 showed that when initial pH $(pH)_i$ was adjusted to 1, pH_f remained almost constant and the adsorption of Pb(II) was least (10%) because of the electrostatic repulsion between positively charged adsorbent surface and positively charged Pb^{2+} ions since adsorbent surface was protonated due to the presence of excess H^+ ions [Zou et al., 2006; Rout et al., 2013]. When pH_i was adjusted to 2, the adsorption of Pb(II) increased to 42%, possibly due to a little less competition of Pb^{2+} with H^+ ions. However, when pH_i was adjusted to 4, the pH_f value increased to 6 at equilibrium and at the same time, the adsorption of Pb(II) increased to maximum (96%) possibly as a result of the adsorption of Pb^{2+} ions along with H^+ ions. When pH_i was further increased to 6, the pH_f remained unaltered ($pH_f = 6.5$) but adsorption of Pb(II) decreased slightly (95%). A similar trend continued when pH_i was further increased and adsorption of Pb(II) decreased to 84% and pH_f also reduced to a value of 7.5 at $pH_i = 10$ (Fig. 2.6). The decrease in the equilibrium pH (pH_f) and adsorption of Pb(II) at pH > 6 can be explained on the basis of Pb(II) speciation at different pH values. Pb(II) is present in the forms of Pb^{2+} (pH 2-4);

$Pb(OH)^+$ (pH 4-6); $Pb(OH)_2$ (pH 6-10); and $Pb(OH)^-_3$ (pH 10-12) [Tan et al., 2008; Pourreza et al., 2014]. It can therefore be concluded that Pb(II) was adsorbed as Pb^{2+} ions up to pH 4 and above this pH Pb(II) was adsorbed in the form of various hydroxide Pb(II) species [Yongjie et al., 2009, Rao et al., 2012a] in the form of micro precipitation. Further, the formation of hydroxide species of Pb(II) started above pH 6 hence pH_f decreased due to excess H^+ ions remaining in the solution.

$$Pb^{2+} + H^+ + OH^- \rightarrow Pb(OH)^+ + H^+ \quad (6)$$

$$Pb^{2+} + 2H_2O \rightarrow Pb(OH)_2 + 2H^+ \quad (7)$$

The effect of electrolyte (KNO_3) on the adsorption of Pb(II) was also studied and it was found that adsorption was decreased in presence of 0.1 N KNO_3 because of the competitive effect of K^+ ions. The effect of electrolyte was more pronounced below pH 4 (Fig. 2.6) but at pH 4 and above, the adsorption of Pb(II) was not affected perhaps due to the fact that below pH 4 both H^+ and K^+ ions screen the electrostatic attraction between negatively charged adsorbent surface and positively charged Pb(II) ions but above pH 4 the effect of H^+ ions (extremely low concentration) was reduced to much extent and hence adsorption of Pb(II) was not much influenced in presence of electrolyte alone. The pH_{PZC} (point of zero charge) of the adsorbent surface was found to be 4 (Fig. 2.7), indicating that adsorbent surface was positive at pH< 4; neutral at pH = 4 and negatively charged at pH > 4 [Rout et al., 2013].

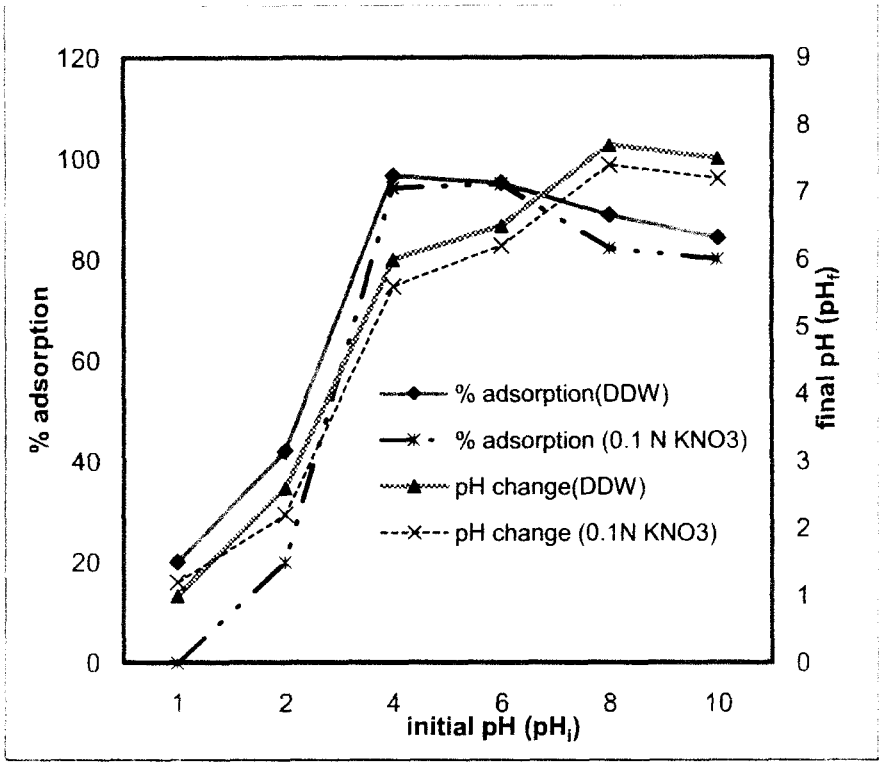


Fig 2.6: Effect of pH and electrolyte on the adsorption of Pb(II) onto TAFP
(conditions; adsorbent = 0.2g; Pb(II) = 50 mg.L^{-1}temp = 30°C)

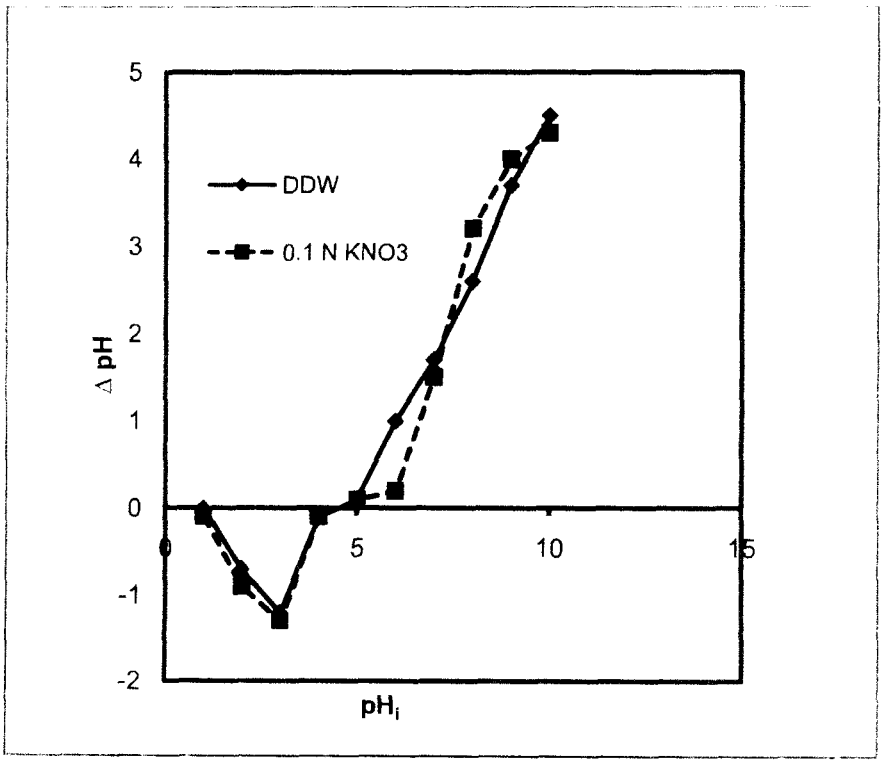


Fig 2.7: Point of zero charge

2.3.4. Effect of adsorbent dose

The effect of adsorbent dose on adsorption capacity and percent adsorption of Pb(II) by varying the dose of TAFP is shown in the Fig. 2.8. Percent adsorption increased while adsorption capacity, q_e ($mg.g^{-1}$) decreased when adsorbent dose increased from 0.1-1.0 g. This increase in the percent adsorption of Pb(II) might be due to the fact that on increasing the adsorbent dose, number of sites available for adsorption also increased[Baniamerian et al., 2009; Wang et al., 2013]. The maximum adsorption of Pb(II) was about 99.4% at 1g dose. The decrease in adsorption capacity with increasing adsorbent dose might be due to the fact that some of the adsorption sites were remain unsaturated during the adsorption process [Rao et al., 2007] or some of the adsorbent particles interact with each other to form aggregates which reduced the total surface area of the adsorbent [Yongjie et al., 2009; Rao et al., 2012b].

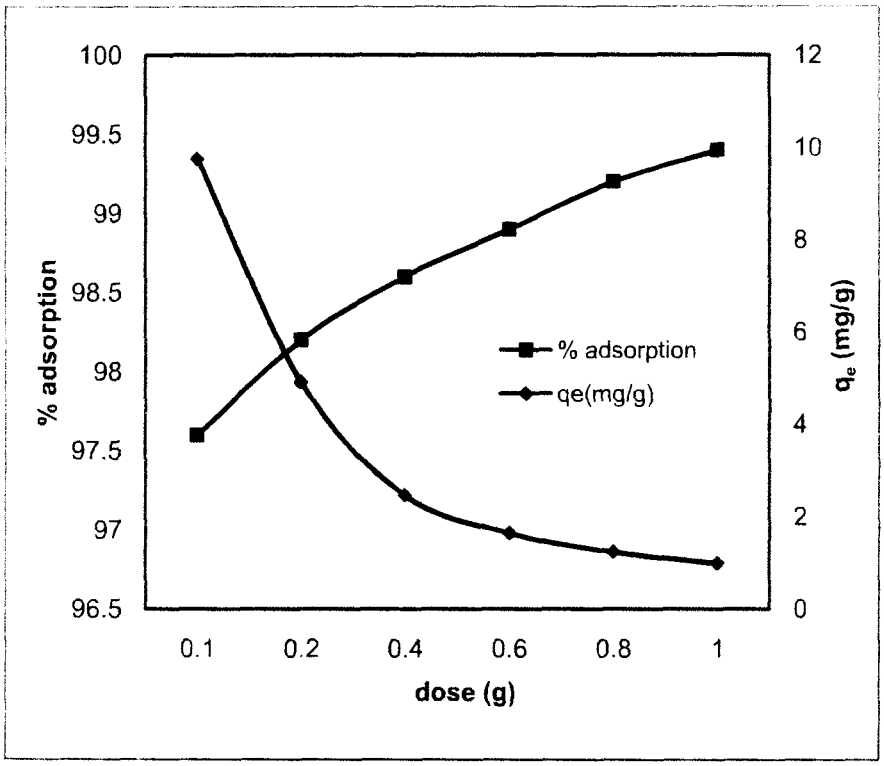


Fig 2.8: Effect of doses on the adsorption of Pb(II) onto TAFP

(Conditions; Pb(II) = 50 $mg.L^{-1}$; pH = 4; temp = 30°C)

2.3.5. Adsorption isotherms

The equilibrium adsorption isotherm is fundamentally very crucial in designing adsorption systems. In general, an adsorption isotherm is an invaluable curve describing the phenomenon governing the retention (or release) or mobility of a substance from the aqueous phase to a solid-phase at a constant temperature and pH [Allen et al., 2004; Limousin et al., 2007; Foo et al., 2010]. The Langmuir, Freundlich, Temkin and Dubinin–Radushkevich (D–R) models were used to fit the experimental data for the adsorption of Pb(II) at 30, 40 and 50°C. The results obtained are reported in Table 2.4. In order to evaluate the fitness of the data, the values of the correlation coefficient (R^2), were evaluated for each model.

Langmuir adsorption isotherm describes quantitatively the formation of monolayer on the surface of the adsorbent. The model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface [Dada et al., 2012]. The linear form of the Langmuir model may be written as:

$$\frac{1}{q_e} = \frac{1}{q_m} \times \frac{1}{b} \times \frac{1}{C_e} + \frac{1}{q_m} \qquad (8)$$

where C_e is the equilibrium concentration of Pb(II) in the solution ($mg.L^{-1}$), q_e is the amount of Pb(II) adsorbed per unit weight of adsorbent ($mg.g^{-1}$), q_m is the amount of Pb(II) required to form a monolayer ($mg.g^{-1}$), or the maximum monolayer adsorption capacity, and b is a constant related to the energy of adsorption ($L.mg^{-1}$). The values of b and q_m can be calculated from the slope and intercept of the linear plots of $1/q_e$ versus $1/C_e$ at different temperatures (Fig. 2.9). The coefficient b in Langmuir equation is a measure of the stability of the complex formed between metal ions and adsorbent under specified experimental conditions [Ayranci et al., 2005; Rao et al., 2007]. The data obtained from the model were best fitted at 30°C as indicated by high correlation coefficient value (R^2= 0.999) (Table 2.4).

Freundlich adsorption isotherm is commonly used to describe the adsorption characteristics for the heterogeneous surface [Hutson et al., 2000; Dada et al., 2012]. The linear form of the Freundlich model can be written as:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (9)$$

Where, K_F and n are the Freundlich constants. The constant K_F $(mg.g^{-1})(L.mg^{-1})^{1/n}$ is an approximate indicator of adsorption capacity, while 1/n is a function of the strength of adsorption in the adsorption process [Voudrias et al., 2002]. The data obtained from this model (Fig. 2.10) indicated that the values of K_F and n increased as the temperature increased from 30 to 50°C. The values of n lies between 1 and 10, indicated favourable adsorption [Goldberg, 2005]. The data also revealed that Freundlich isotherm was best obeyed at 30°C ($R^2 = 0.999$)

The Temkin isotherm contains a factor that explicitly taking into the account of adsorbent–adsorbate interactions. By ignoring the extremely low and large value of concentrations, the model assumes that heat of adsorption (function of temperature) of all molecules in the layer would decrease linearly rather than logarithmic with coverage [Dada et al., 2012]. The linear form of the Temkin equation can be written as:

$$q_e = \left(\frac{RT}{b}\right) \ln A + \left(\frac{RT}{b}\right) \ln C_e \quad (10)$$

Or,

$$q_e = B \ln A + B \ln C_e \quad (11)$$

Where, (RT/b) = B, R is the universal gas constant ($J.mol^{-1}.K^{-1}$), T is the absolute temperature (K) and b is a constant. The quantities A ($g.L^{-1}$) and B ($J.mol^{-1}$) are Temkin constants related to the adsorption potential and the heat of adsorption, respectively. The values of A and B can be calculated from the slope and intercept of the plot of q_e versus ln C_e (Fig. 2.11). The data obtained from the Temkin model (Table 4) indicated that this model was best fitted at 30 °C ($R^2 = 0.991$).

Dubinin–Radushkevich isotherm is generally applied to express the adsorption mechanism with a Gaussian energy distribution onto a heterogeneous surface [Dabrowski et al., 2001; Gunay et al., 2007, Dada et al., 2012]. The linear form of this equation is represented as;

$$\ln q_e = \ln q_m - \beta\varepsilon^2 \quad (12)$$

Where, ε is the Polanyi potential ($J.mol^{-1}$), q_m is the monolayer capacity ($mol.g^{-1}$), C_e is the equilibrium concentration ($mol.L^{-1}$) and β is a constant related to the adsorption energy ($mol.K^{-2}.J^{-2}$). The Polanyi potential (ε) and the mean free energy of adsorption (E, $kJ.mol^{-1}$) can be calculated from the following equations;

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \quad (13)$$

And

$$E = \frac{1}{(2\beta)^{1/2}} \quad (14)$$

The D-R constants q_m and β were evaluated from the linear plots of ln qe versus ε^2(Fig. 2.12). The constant β gives an idea about the mean free energy E ($kJ.mol^{-1}$) of adsorption. The values of E ($KJ.mol^{-1}$) obtained lies between 8 and 16 kJ mol^{-1} showed that the adsorption was chemical in nature [Rao et al., 2010]. The data listed in Table 4 indicated that all the above models gave a good fit to the experimental data obtained at 30 °C, with the R^2 values for all the models being greater than 0.99.

Table 2.4: Adsorption isotherm parameters at different temperatures

Isotherm	Parameters	30°C	40°C	50°C
Langmuir	B ($L\ mg^{-1}$)	0.2743	1.0556	2.3115
	q_m ($mg\ g^{-1}$)	27.390	13.850	11.820
	R^2	0.9993	0.8795	0.9506
Freundlich	K_F ($mg.g^{-1}$) $(L.mg^{-1})^{1/n}$	5.8425	7.0372	8.3291
	n	1.3450	1.698	2.2230
	R^2	0.9994	0.9031	0.9766
Temkin	A ($L.g^{-1}$)	3.105	5.873	14.546
	B ($J.mol^{-1}$)	5.264	4.108	3.1620
	R^2	0.9917	0.8481	0.9397
D-R	q_m (($mol\ g^{-1}$)	2.967×10^{-3}	1.324×10^{-3}	0.562×10^{-3}
	β ($mol\ k^{-2}\ J^{-2}$)	4.896×10^{-9}	3.608×10^{-9}	2.441×10^{-9}
	E ($kJ\ mol^{-1}$)	10.106	11.772	14.312
	R^2	0.9996	0.9021	0.9704

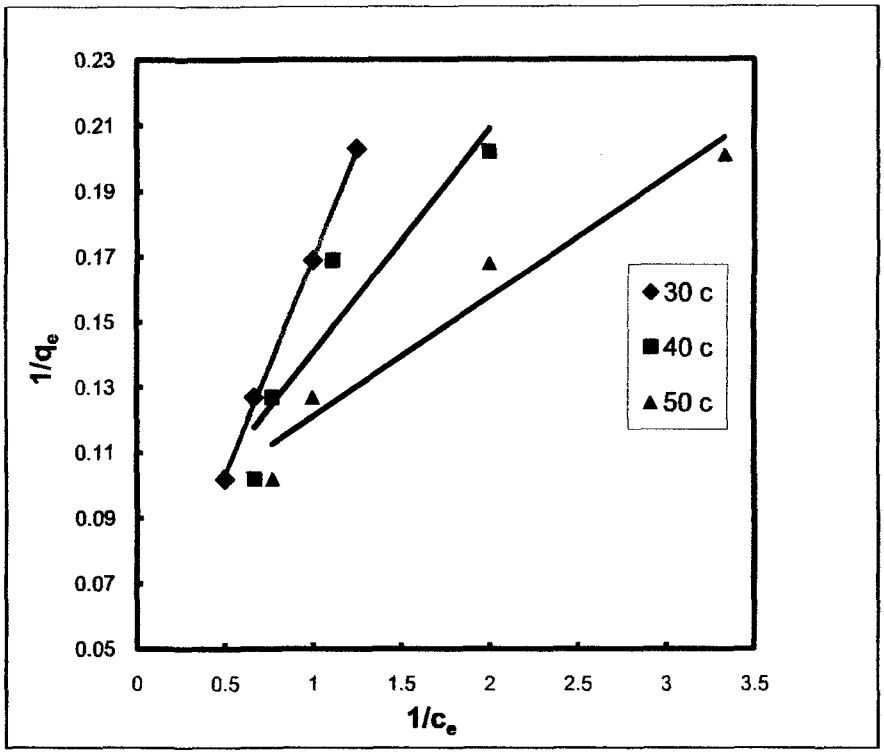


Fig 2.9: Langmuir isotherm for the adsorption of Pb(II) onto TAFP at different temperature

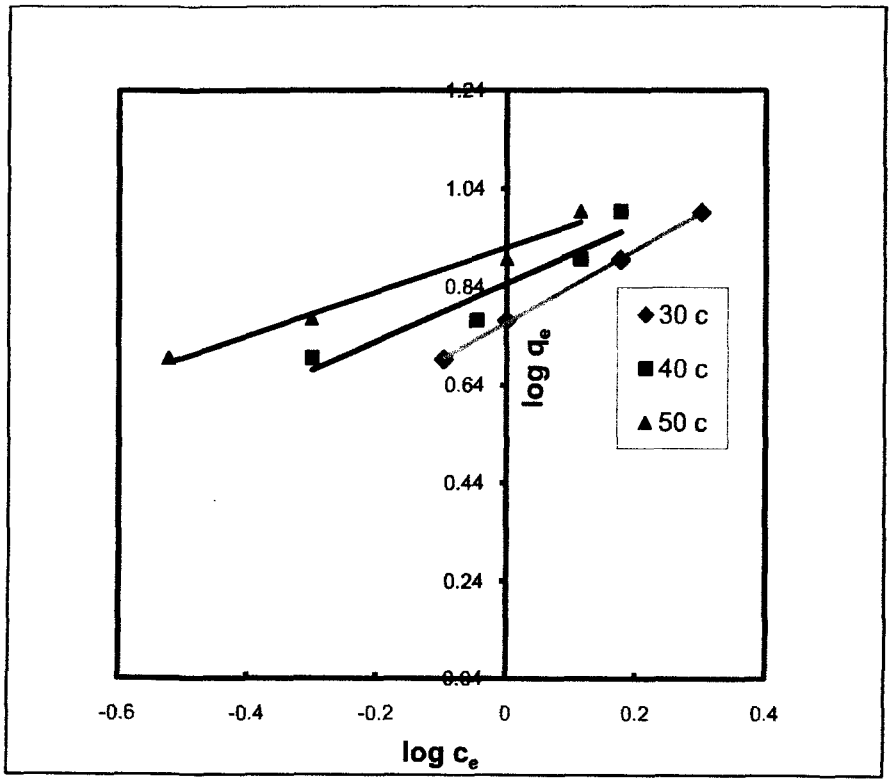


Fig 2.10: Freudlich isotherm for the adsorption of Pb(II) onto TAFP at different temperature

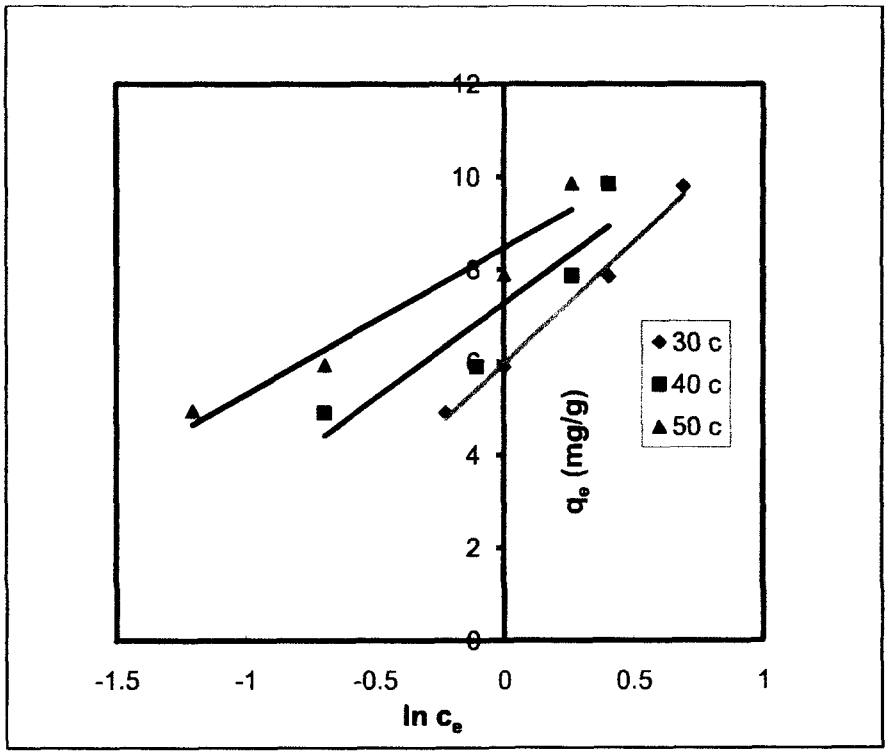


Fig 2.11: Temkin isotherm for the adsorption of Pb(II) onto TAFP at different temperature

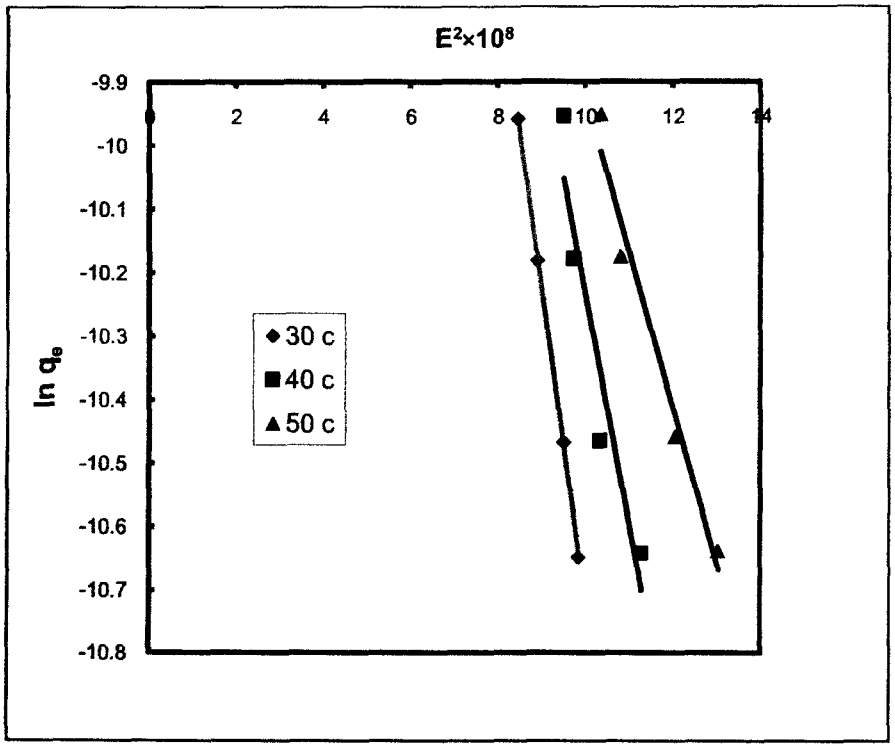


Fig 2.12: D-R isotherm for the adsorption of Pb(II) onto TAFP at different temperature

2.3.6. Adsorption thermodynamics

Thermodynamic studies were conducted because they can provide information on inherent energetic changes. The effect of temperature on the adsorption of Pb(II) ions was studied over the temperature range of 30–50°C. The thermodynamic parameters such as enthalpy change (ΔH^{o}) and entropy change (ΔS^{o}) were obtained from the Van't Hoff equation [Rao et al., 2007].

$$\log K_c = \frac{\Delta S^{o}}{2.303R} - \frac{\Delta H^{o}}{2.303RT} \qquad (15)$$

ΔS^{o} and ΔH^{o} were calculated from the slope and intercept of linear plot of log Kc versus 1/T (Fig. 2.13). Equilibrium constant (K_c) was calculated from the following relationship [Rao et al., 2007].

$$K_c = \frac{C_{Ac}}{C_e} \qquad (16)$$

Where, C_{Ac} and C_e are the equilibrium concentration of Pb(II) ions on the adsorbent and in the solution, respectively. Standard Gibb's free energy change (ΔG^{o}) was then calculated from the equation.

$$\Delta G^{o} = -RT \ln K_c \qquad (17)$$

Where, T is the absolute temperature (K) and R is the gas constant ($J.mol^{-1}.K^{-1}$). The values obtained for the various thermodynamic parameters are listed in Table 2.5.The positive value of ΔH^{o} suggested endothermic nature of adsorption of Pb(II) on TAFP. The values of ΔG^{o} were found to be negative at all temperatures which indicated that the process was spontaneous and spontaneity increased with increase in temperature as indicated by decreasing ΔG^{o} values. The positive value of ΔS^{o} suggested increasing randomness at the solid/liquid interface during the adsorption process.

Table 2.5: Thermodynamic parameters for the adsorption of Pb(II) on TAFP at different temperatures

Temperature (°C)	K_C	ΔG^0 (kJ mol^{-1})	ΔH^0 (kJ mol^{-1})	ΔS^0 (kJ mol^{-1} K^{-1})	R^2
20	040.67	-09.027			
30	061.50	-10.376			
40	099.00	-11.958	39.002	0.163	0.9977
50	165.67	-13.722			

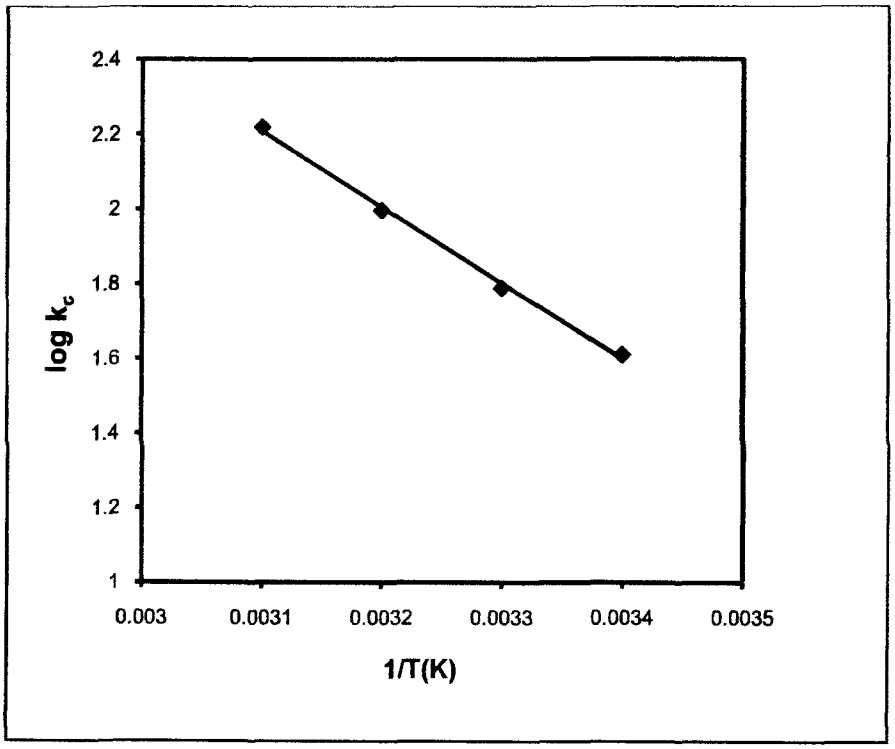


Fig 2.13: Van't Hoff plot

2.3.7. Adsorption kinetics

The evaluation of kinetic models is an important aspect for designing and optimization of water and wastewater treatment process. Adsorption kinetic models correlate the adsorbate uptake rate from bulk concentration of the adsorbate [Subha et al., 2009; Azarudeen et al., 2013]. To investigate the mechanism of adsorption and rate controlling steps, the kinetic data were analyzed using Pseudo-first order, Pseudo-second order and intra-particle diffusion models. A pseudo-first-order kinetic model as expressed by Lagergen [Li et al., 2013] can be written as:

$$\log (q_e - q_t) = \log q_e - \left(\frac{K_1}{2.303}\right) x\ t \qquad (18)$$

Where q_e and q_t are the amount of metal adsorbed ($mg.g^{-1}$) at equilibrium and at time t, respectively and K_1 is the pseudo-first order equilibrium rate constant (min^{-1}). A plot of $\log(q_e - q_t)$ versus t gave straight line over a wide range of initial Pb(II) concentrations (Fig. 2.14). However values of q_e calculated ($q_{e(cal)}$) from this model differed appreciably from the values of q_e obtained experimentally ($q_{e(exp)}$), indicating that the adsorption process did not follow the pseudo first order rate equation (Table 6).

Pseudo-second-order adsorption rate equation [Ho et al., 1998] may be expressed as;

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right) x\ t \qquad (19)$$

Where, K_2 is the pseudo-second-order adsorption rate constant ($g.mg^{-1}.min^{-1}$). A plot of t/q_t versus t gave straight line for all experimental concentrations (Fig. 2.15). The values of q_e and K_2 were calculated from the slope and intercept, respectively. The initial adsorption rate h ($mg.g^{-1}.min^{-1}$) was calculated from the relation [Ho et al., 2003].

$$h = k_2 x q_e^2 \qquad (20)$$

The values of q_e, h, K_2 and R^2 are listed in Table 2.6. When The values of $q_{e(cal)}$ were compared with $q_{e(exp)}$, it was found that both the values were in good agreement for all experimental concentrations. Moreover the correlation coefficient (R^2) values were also found to be very close to 1, thus it can be concluded that pseudo-second order model was well fitted with the experimental data. It can also be seen from Table 6 that with the increase in initial concentration of Pb(II), the rate constant (K_2) decreased. A similar observation was also reported by earlier researchers [Yao et al., 2010].

Kinetic data were also analyzed using the Weber and Morris [Volesky et al., 2003] intra-particle diffusion model which can be expressed as

$$q_e = k_{id} \, x \, t^{1/2} + I \qquad (21)$$

Where K_{id} is the intra-particle diffusion rate constant ($mg.g^{-1}.min^{-1)}$ and I is the intercept ($mg.g^{-1}$) which gives an idea about the thickness of a boundary layer, q_t is the amount of Pb(II) ions adsorbed ($mg.g^{-1}$) at time t (min). Fig. 2.16 shows the plots of q_t versus $t^{1/2}$ for different initial Pb(II) concentrations. The values of K_{id}, I and R^2 are listed in Table 2.7. The R^2 values (between 0.8304 and 0.9739) suggested that adsorption of Pb(II) can be followed by intra-particle diffusion model. The deviation in the plots from origin for all concentrations indicated that intra-particle diffusion is not the only rate-controlling step but some other processes like film diffusion and pore diffusion were also involved in the adsorption process. The increase in intercept values with increase in concentration is indicative of increased boundary layer effect [Godhana et al., 2008].

Table 2.6: Pseudo-first order and pseudo-second order kinetics constants for the adsorption of Pb (II) on TAFP

Concentration(mg L^{-1})	$q_{e(exp)}$ (mg g^{-1})	Pseudo-first-order kinetics			Pseudo-second -order kinetics			
		$q_{e(cal)}$ (mg g^{-1})	K_1 (min^{-1})	R^2	$q_{e(cal)}$ (mg g^{-1})	K_2 (g mg^{-1} min^{-1})	h (g mg^{-1} min^{-1})	R^2
10	0.95	0.4268	0.7026	0.7312	0.95	13.078	011.905	0.9989
20	1.92	0.5253	1.0822	0.9176	1.92	15.674	058.166	0.9999
50	4.91	0.5385	0.4214	0.9332	4.92	04.005	097.093	1.0000
60	5.90	0.2378	0.1829	0.5987	5.89	05.130	178.571	1.0000
80	7.85	0.5623	0.1829	0.8971	7.86	02.078	128.206	1.0000
100	9.80	0.4991	0.1179	0.7353	9.79	01.533	147.059	1.0000

Table 2.7: Intra-particle diffusion parameters for the adsorption of Pb(II) on TAFP

Concentration (mg L^{-1})	K_{id} (mg g^{-1} $min^{-1/2}$)	I (mg g^{-1})	R^2
10	0.0751	0.7822	0.9739
20	0.0779	1.7554	0.9095
50	0.0604	4.6941	0.9174
60	0.0262	5.7795	0.8636
80	0.0428	7.6335	0.8304
100	0.0372	9.5851	0.9296

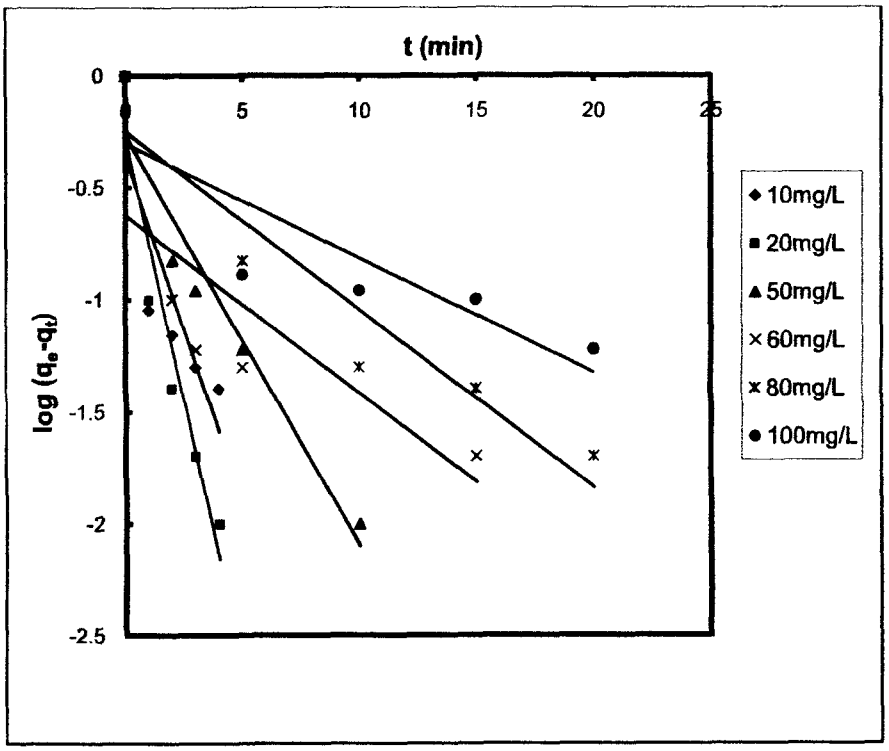


Fig 2.14: Pseudo-first order kinetics model (conditions; pH = 4; adsorbent = 0.2g; temp = 30°C)

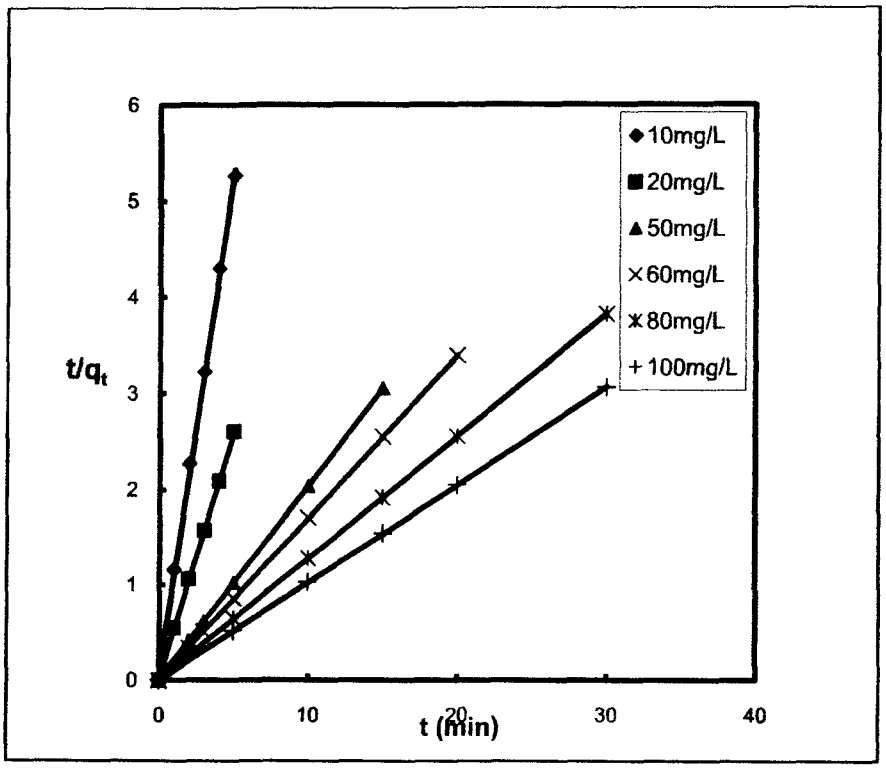


Fig 2.15: Pseudo-second order kinetics model (conditions; pH = 4; adsorbent = 0.2g; temp = 30°C)

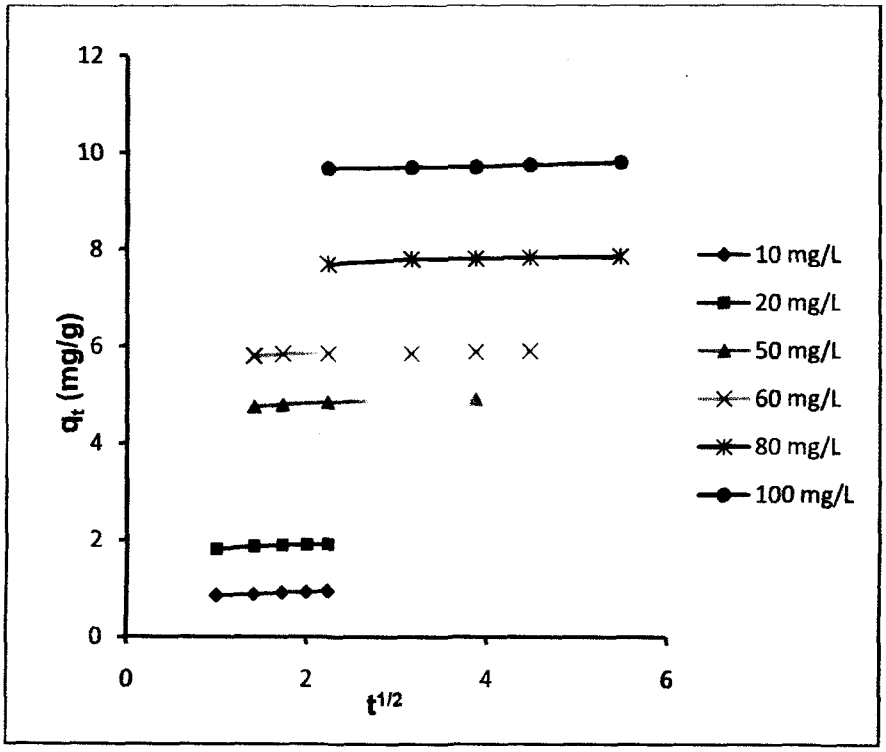


Fig 2.16: Intra-particle diffusion model (conditions; pH = 4; adsorbent = 0.2g; temp = 30°C)

2.3.8. Breakthrough capacity

Determination of breakthrough capacity is an important aspect in process design as it directly affects the feasibility and economics of the process [Gupta et al., 2001, Rao et al., 2012] Breakthrough capacity can be determined by making use of the concentration gradient between the solute adsorbed by the adsorbent and that remaining in the solution. The column is operational until the metal ions in the effluent start appearing and for practical purposes the working life of the column is over, called breakthrough point. The breakthrough curve (Fig. 2.17) indicated that 50 mL of Pb(II) solution could be passed through the column without detecting Pb(II) ions in the effluent. The breakthrough and exhaustive capacities were found to be 5 and 15 $mg.g^{-1}$ respectively.

2.3.9. Desorption studies

In order to explore the practical utility of the adsorbent, desorption of Pb(II) was carried out by column process. In this study, aqueous solution of HCl was used as the desorbing agent because of its economic feasibility [Kwon et al., 2012; Liu et al., 2014]. Desorption studies were carried out by using the spent column obtained from breakthrough experiment. Thus, in a breakthrough capacity experiment, it was found that a total of 7.13 mg of Pb(II) ions were retained when 250 mL of Pb(II) ion solution of concentration 50 $mg.L^{-1}$ was passed through the column. For desorbing Pb(II) ion from TAFP, 0.05M HCl solution was passed through this column and the effluent was collected in 10 mL fractions. A total of 6.0 mg Pb(II) ions (84%) was recovered upon elution within 30 mL of the effluent (Fig. 2.18).

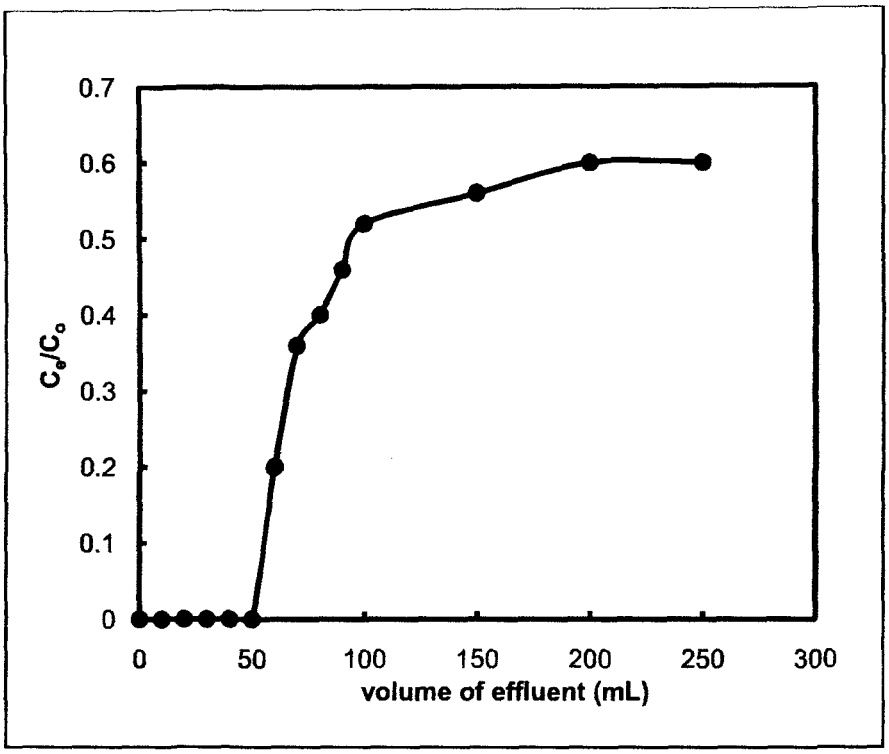


Fig 2.17: Breakthrough curve (conditions; adsorbent = 0.5g; Pb(II) = 50 mg.L^{-1} ; flow rate = 1mL.min^{-1})

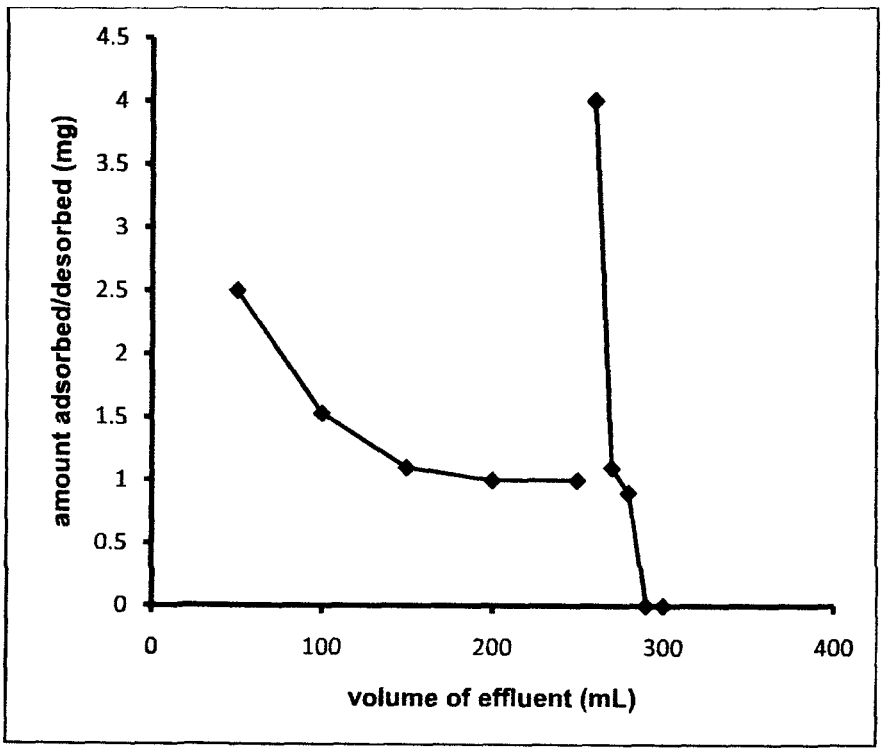


Fig 2.18: Adsorption and desorption of Pb (II) by column process (conditions; adsorbent = 0.5g Pb(II) = 50 mg.L^{-1}; flow rate = 1mL.min^{-1})

2.4. CONCLUSIONS

Terminalia arjuna is a medicinal plant and is used in ayurveda, siddha and unani system of medicine. The adsorption properties of *Terminalia arjuna* have been explored using batch process. The adsorption of Pb(II) ions was pH-dependent with maximum adsorption(96%) occurring at pH 4. Presence of electrolyte (KNO_3) in the solution has negligible effect on the adsorption of Pb(II). Therefore it can be concluded that the maximum amount of Pb(II) can be removed from aqueous solution even in presence of electrolyte without any significant loss of adsorption capacity. Kinetic data showed that pseudo-second order rate equation was followed by the system since qe values calculated from the model were very close to q_e determined experimentally. The fitting of the data in Langmuir, Freundlich, Temkin and D–R isotherms indicated that these models were best obeyed at 30°C as indicated by their correlation coefficient (R^2), The maximum monolayer adsorption capacity was found to be 27.39 $mg.g^{-1}$. The magnitude of the mean free energy indicates that adsorption of Pb(II) occured via chemisorption. The thermodynamic parameters ΔH^0 and ΔG^0 indicated that the adsorption process was endothermic and spontaneous. Adsorption was fast and equilibrium was reached within 30 min over a wide range of Pb(II) concentration. Breakthrough studies showed that with Pb(II) concentrations of 50 $mg.L^{-1}$, 50 mL of the effluent could be passed through the column without detecting Pb(II) ions. Desorption studies were carried out by column method using 0.05M HCl as desorbing solution and it was found that 84% of Pb(II) could be recovered within 30 mL effluent.

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